

Final
NBSIR 80-2142 (Aluminum Association)

Plating on Aluminum

FILE COPY

AUG 5 1981

D. S. Lashmore

Corrosion and Electrodeposition Group
Chemical Stability and Corrosion Division
National Measurement Laboratory
U.S. Department of Commerce
National Bureau of Standards
Washington, DC 20234

November 1980

Final Report

Prepared for

The Aluminum Association
818 Connecticut Avenue, N.W.
Washington, DC 20006

The American Electroplaters Society
1201 Louisiana Ave.
Winter Park, FL 32789

PLATING ON ALUMINUM

D. S. Lashmore

Corrosion and Electrodeposition Group
Chemical Stability and Corrosion Division
National Measurement Laboratory
U.S. Department of Commerce
National Bureau of Standards
Washington, DC 20234

November 1980

Final Report

Prepared for
The Aluminum Association
818 Connecticut Avenue, N.W.
Washington, DC 20006

The American Electroplaters Society
1201 Louisiana Ave.
Winter Park, FL 32789



U.S. DEPARTMENT OF COMMERCE, Philip M. Klutznick, *Secretary*
Jordan J. Baruch, *Assistant Secretary for Productivity, Technology, and Innovation*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

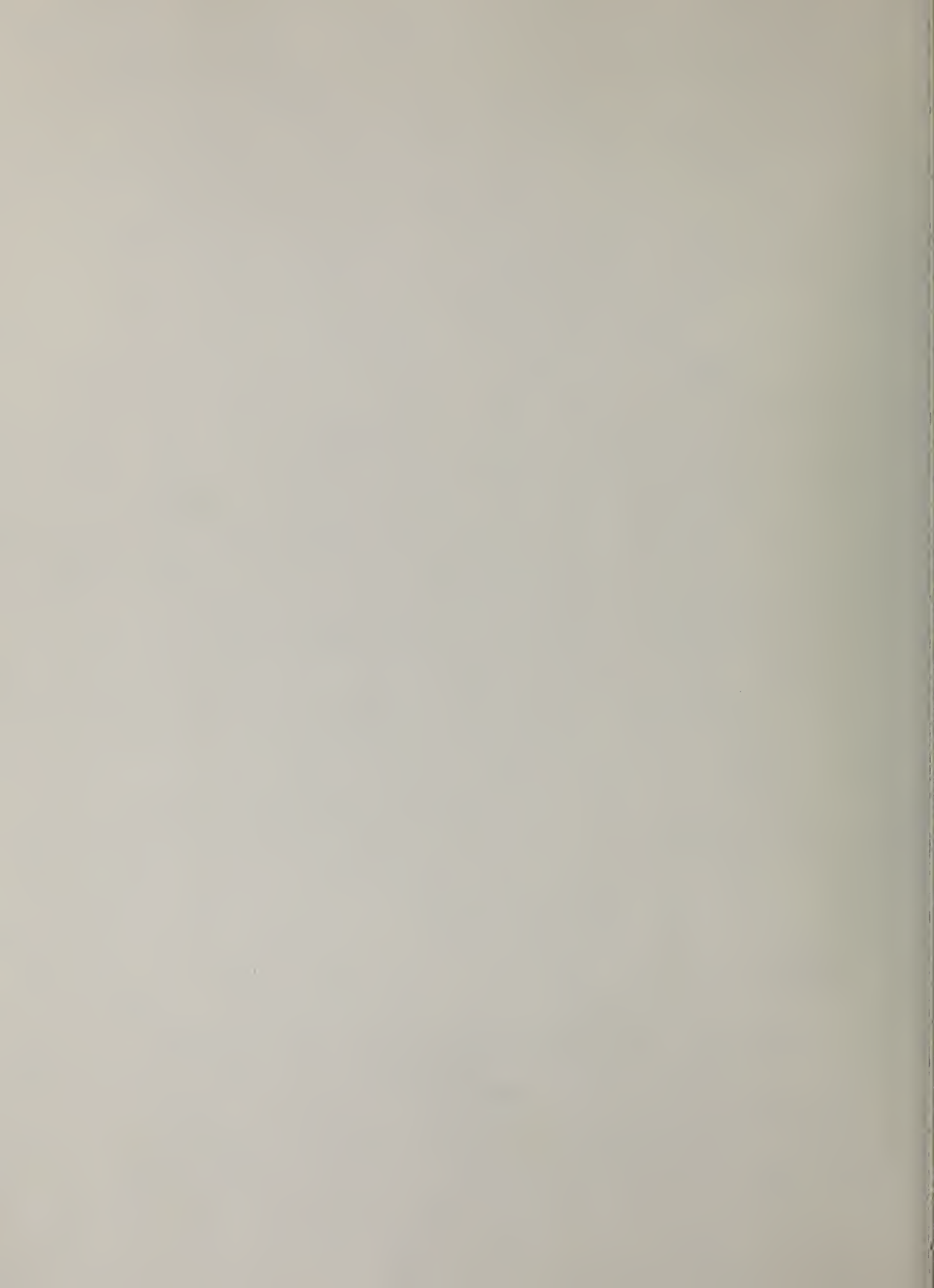


Table of Contents

	Page
1. Introduction	1
2. Program Summary	2
3. Phosphoric Acid Anodizing Prior to Plating	10
3.1. Adhesion Data	10
3.2. Microstructure of the Anodic Film	17
3.2.1. Microstructure of nickel plated onto the anodic film	19
3.2.2. Initial Stages of Oxidation	25
3.3. Electrochemical Measurements	32
3.3.1. Current Density versus Applied Potential	32
3.3.2. Scanning Voltammetry	33
4. Immersion Deposition	37
4.1. Scanning Voltammetry	37
4.2. Dissolution Data	41
4.3. Discussion	44
5. Adhesion Theory	45
5.1. Adhesion of Metallic Coatings	45
5.2. Pre-existing Crack--Griffith Criterion	52
5.3. Psuedomorphism: the critical radius and the critical thickness	56
List of Figures	61
References	36, 60

1. Introduction:

This report covers the period from about July 1979 to February 1980 and includes, not only a discussion of work on both anodizing and immersion deposition, but also a summary of the results obtained over the last three years. A general theory of adhesion of metal coatings on metal substrates has been developed and adhesive energies were calculated for epitaxial zinc on aluminum. The case of a preexisting crack in the interface was considered.

The work on anodizing has resulted in a greatly improved understanding of adhesion mechanisms. The morphology of the initial stages of anodic film formation on aluminum alloy 7146-T6 has been characterized, yielding results rather different than predicted from commonly accepted theories. The morphology of nickel deposited into the pores of the anodic film has been characterized for the first time, it is believed, by direct TEM studies of cross sections of bulk specimens on which adhesion measurements have been made.

2. Program Summary:

The reader is urged to refer to particular progress reports and to Plating 67, 37 (1980) and the Journal of the Electrochemical-Society 127, 573 (1980) for more complete information on the first two years' results. During the three years that the Aluminum Association project Decorative Chrome Plating of Aluminum has been carried out, three major areas have been worked on: immersion deposition, anodizing, and the theory of adhesion between metal coatings and substrates. A summary of the results follows:

2.1. Immersion Deposition:

2.1.1. Substrate Orientation:

It was shown in Progress Reports (P. R.) II-IV that the substrate crystal structure plays an important role in both the zincate and stannate processes. The dissolution of the aluminum in the caustic zincate solutions is a sensitive function of the crystallographic orientation. Moreover, zinc was shown to form epitaxial deposits on all aluminum principal planes. The bronze in the stannate process was shown to exhibit a strong preferred orientation.

2.1.2. Cleaning Process:

In virtually every process for immersion deposition, a caustic cleaning step is specified. The highly deformed surface usually present on most material interferes with epitaxial phenomena. In addition, this highly deformed layer would be expected to dissolve more rapidly than less deformed material, permitting a thick zinc deposit to form preferentially at regions of high deformation. The etch cleaning step not only removes the highly deformed material but also

attacks the same families of planes as the zincate and stannate electrolytes. This step is a necessity, if the balance between aluminum dissolution and uniform zinc deposition is to be maintained.

2.1.3. Alloy Constituents:

It was shown that even small traces of magnesium determine the sites at which large zinc crystallites grow. The epitaxial phenomena observed on pure aluminum were also observed on one alloy (6061-T6) and probably exist on others (P. R. II & III). Investigations of adhesion correlations with alloying constituent were discussed in P. R. IV. Pure aluminum exhibited greater adhesion than did the alloys investigated here.

2.1.4. Effect of Ferric Chloride and Rochelle Salts:

It was shown that small additions of ferric chloride and Rochelle salts have a major effect on the deposition process. When absent, it was shown that three atoms of zinc are deposited for every two atoms of aluminum dissolved. When present, it was shown that almost nine atoms of aluminum are dissolved for each atom of zinc deposited. (See P. R. II.) It was shown that iron is deposited (by immersion or perhaps chemisorption) before the bulk of the zinc. Following a nitric acid immersion (the double zincate procedure), it was shown by Rutherford back scattering experiments (P. R. III) that about two monolayers of iron and two monolayers of zinc were left on the surface. Transmission electron microscopy of double zincated specimens indicated the existence of an iron zinc alloy formed just at the aluminum surface. (See P. R. I-IV.)

2.1.5. Morphology:

The morphology of immersion deposits was characterized by optical, SEM and TEM techniques, both on pure aluminum and on a number of alloys. See P. R. I-IV, Plating 67, 37 (1980), and J. Electrochem. Soc. 127, 573 (1980). Zinc forms epitaxial deposits on the aluminum substrates so that Zn:

$(0001) < \bar{1}0\bar{1}0 > // Al (100) < 010 >$, Zn:

$(0001) < \bar{1}1\bar{2}0 > // Al (111) < \bar{1}\bar{1}0 >$ and Zn:

$(0001) < \bar{1}1\bar{2}0 > // Al (\bar{1}\bar{1}0) < 111 >$.

2.1.6. The Stannate Process:

It was shown by TEM that tin crystallites cover the surface following the stannate immersion process. The tin was shown to deposit in three distinct morphologies (See P. R. II.): (1) the formation of a fine grained deposit ($< 20\text{\AA}$) completely covering the surface; (2) at a later time, the formation of small crystallites in discrete areas; and, finally, (3) the growth of large, almost spherical clusters. It seems that stage III is just barely reached after about 45 seconds in the electrolyte.

The bronze layer deposited as part of the stannate process was shown to exhibit a strong preferred orientation. However, extensive work on this phenomenon was not done because of the proprietary nature, of the commercial process of which it is a part.

Significantly, it was shown that there are important adhesion variations from the top to the bottom of vertically

plated specimens. The greatest adhesion occurred on the lower part. Apparently, this phenomenon was also revealed in the field by corrosion variations on plated bumpers.

Adhesion on a number of alloys was characterized by peel testing. Deposition on single crystal spheres indicated that a similar deposition mechanism existed with the zincate process, (P. R. II, III & IV).

2.1.7. Field Ion Microscopy (F.I.M.)

Techniques were developed to image zinc coated aluminum in the F.I.M. (see P. R. IV). The zinc was observed to form blade shaped deposits on the aluminum tips, probably due to selective deposition on certain crystallographic planes.

2.1.9. Scanning Voltammetry and Acid Dissolution Data:

Scanning voltammetric data indicated that the deposition of an iron-zinc or iron layer precedes the deposition of the zinc. By monitoring the substrate potential as a function of time, a modified procedure for depositing a thin layer of zinc or zinc-iron alloy was developed (see Interim Report, Aug. 1979, and section 4.2 of this report).

2.2. Anodizing Pretreatments

2.2.1. Effect of Structure

A procedure was developed to enable direct TEM micrographs of cross sections of anodized aluminum coated with nickel. Apparently, this is the first time that specimens of this type have been prepared, though it should be noted that there has been much published on replicas of anodic films and on

microtomed anodized aluminum. The data shown in this report reveals no penetration of the barrier layer by the nickel, ruling out metallic bonding as an adhesion mechanism.

The initial states of pore formation were characterized by direct TEM studies of anodized 7021-T63 and 7146-T6. The initial stages of growth were shown to be much different from subsequent stages. The anodic oxide seemed to form small square regions which grew together like building blocks on a (100) aluminum substrate (see section 3.2.2 of this report). This evidence indicates the important role played by the structure of the substrate during the initial stages of growth. The classical model of pore growth requires a field assisted dissolution of the aluminum at places where the oxide is thinnest, and such a model is supported by the results obtained during this study. However, in the initial stages of oxide formation the thin areas are not necessarily associated with pore formation; indeed, it was shown that oxide growth can be quite remote from the dissolution sites, as can the initial pore structures.

2.2.2. Effect of Anodizing Parameters on Adhesion:

It was shown that adhesion is an approximately linear function of the applied voltage. Since the cell diameter also increases in a linear manner with the applied voltage, a relationship was thought to exist between adhesion and pore diameter. Moreover, the greater the cell diameter, the less oxide there is per unit area of the coating. This implies that the strength of the oxide itself is the determining

factor (or weak link) in adhesion of subsequent coatings to the anodic film. It should be noted that the pore structure, especially at higher voltages, does not vary much as one changes from one of the three major electrolytes used for this process (sulfuric acid, oxalic acid, and phosphoric acid) to another even though adhesion of subsequent coatings can vary by more than an order of magnitude between the various electrolytes. Therefore, the adhesion does not appear to be dependent upon the pore structure, but, rather, upon the nature of the oxide itself. The composition of the anodic film, varies considerably with the alloy and with the electrolyte.

It was shown (see section 3.1 of this report) that the use of an 0.5 percent solution of HF in place of sulfuric acid on 7146-T6, results in increased adhesion.

2.3. Theory of Adhesion for Metallic Coatings on Metallic Substrates:

2.3.1. A theory of the adhesive energy for metallic:

coatings on metallic substrates was discussed in detail (see section 5 of this report). The theory takes into account the effect of structure through a parameter 'a' which represents the lattice parameter in the interface. This parameter is determined by the orientation of both the substrate crystal and the coating crystal. The adhesive energy as a function only of the structure is

$$E_{ad} = \frac{K G_o a^2}{(2\pi)^2 d} . \quad [1]$$

For f.c.c. materials, $K = 3$, G_0 is the shear modulus in the interface which can be determined from the binding energy between the two metals and d is the distance of closest approach. The lattice parameter in the interface, a , is given by:

$$a = \frac{2a_c a_s}{a_c + a_s} \quad [2]$$

2.3.2. In many cases perfect epitaxy is not possible; therefore, the misfit between the coating and the substrate has to be taken into account. It was shown (see section 5.1 of this report), that the adhesive energy in the case of significant misfit is given by:

$$E_{ad} = \frac{KG_0 a^2}{(2\pi)^2 d} - E_d - E_s \quad [3]$$

where E_d is the dislocation energy per unit area and E_s is the distributed strain energy per unit area. A special case was calculated for zinc coatings on aluminum whose epitaxial relationships were characterized during this program.

2.3.4. The case of a preexisting crack of length $2c$, in the interface was considered, and a Griffith type equation for the minimum stress, $\sigma_{critical}$, necessary to propagate this crack (and thus to cause adhesive failure) was derived as:

$$\sigma_{critical} = \sqrt{\frac{2(\gamma_c + \gamma_s)}{\pi c \left(\frac{1}{E_c} + \frac{1}{E_s} \right)}} \quad [4]$$

This equation will be improved in the future to include the effect of strain energy which may be in many cases an important term.

III. Phosphoric Acid Anodizing Prior to Plating:

3.1. Adhesion Data:

A number of experiments concerned with anodizing of aluminum alloys were performed. A great deal of data has been made available by Wittrock, so the experiments described here were designed to compliment the available literature. The experiments were specifically set up: (a) to characterize the effect on adhesion of variations in the applied anodizing voltage. Surprisingly, no direct data on this subject seems to be available, (b) to examine the effect of post-anodizing treatment on adhesion, and (c) to extend Wittrock's measurements of adhesion as a function of anodizing electrolyte temperature.

3.1.1. Adhesion versus anodizing voltage:

The alloy chosen for this study was 7146-T6 because it is in wide use as a bumper alloy. Studies on 7129-T63 will be reported in the future. Specimens of 5 cm x 10 cm x 0.64 cm were buffed, and degreased with trichloroethylene in an ultrasonic cleaner. Following this treatment, the specimens were further polished with 0.01 μm MgO by hand, given a 30 second treatment in 50 percent nitric acid in an ultrasonic cleaner, rinsed in distilled water, and immediately anodized. The total anodizing charge (for adhesion test specimens) was standardized to about 20 coulombs/cm² regardless of anodizing time. An amp-hour meter was used to monitor the total charge. Following the anodization process, the specimens were given a

post treatment, typically in an electrolyte of 2 g/L sulfamic acid held at 55-60 °C. The specimens were then rinsed in distilled water and placed in a nickel sulfamate electrolyte, maintained at a pH of 2.5 for 60 seconds prior to applying a potential. This potential was increased at a very slow rate in such a way that the current density went from 0 to 4.3 amps/dm² in about 5 minutes. Adhesion was measured by peel testing. All specimens were plated with a 150 μm thickness of nickel.

The adhesion was found to be an approximate linear function of anodizing voltage (figure 1). The extended curves intercept the x-axis at about 15 volts, indicating that 15 V is the threshold below which the adhesion is zero. The slope of the curve, however, changed with the concentration of the acid. The current density versus applied voltage has been superimposed on this data, showing that the greatest adhesion occurs when the current density is about to become unstable. The electrolyte was agitated mechanically. Because the limiting current density is dependent on agitation, the curves shown in figure 1 may not represent the maximum obtainable current density, even though the mixing was quite virorous.

The linear increase of adhesion with anodizing voltage is unexpected if the major bonding forces are Van Der Waals, as thought by Alexsandrov (1), or even if they are due to ionic or covalent bonding. The cell diameter as a function of applied voltage, figure 2 as calculated from the data of Keller, Hunter and Robinson (2). It should be noted that

Figure caption for figure 1 (page 13).

Figure 1. Adhesion and current density as a function of anodizing voltage (a) 10 percent phosphoric acid, 60 °C, (b) three percent phosphoric acid, 60 °C, and (c) 10 percent phosphoric acid, 30 °C.

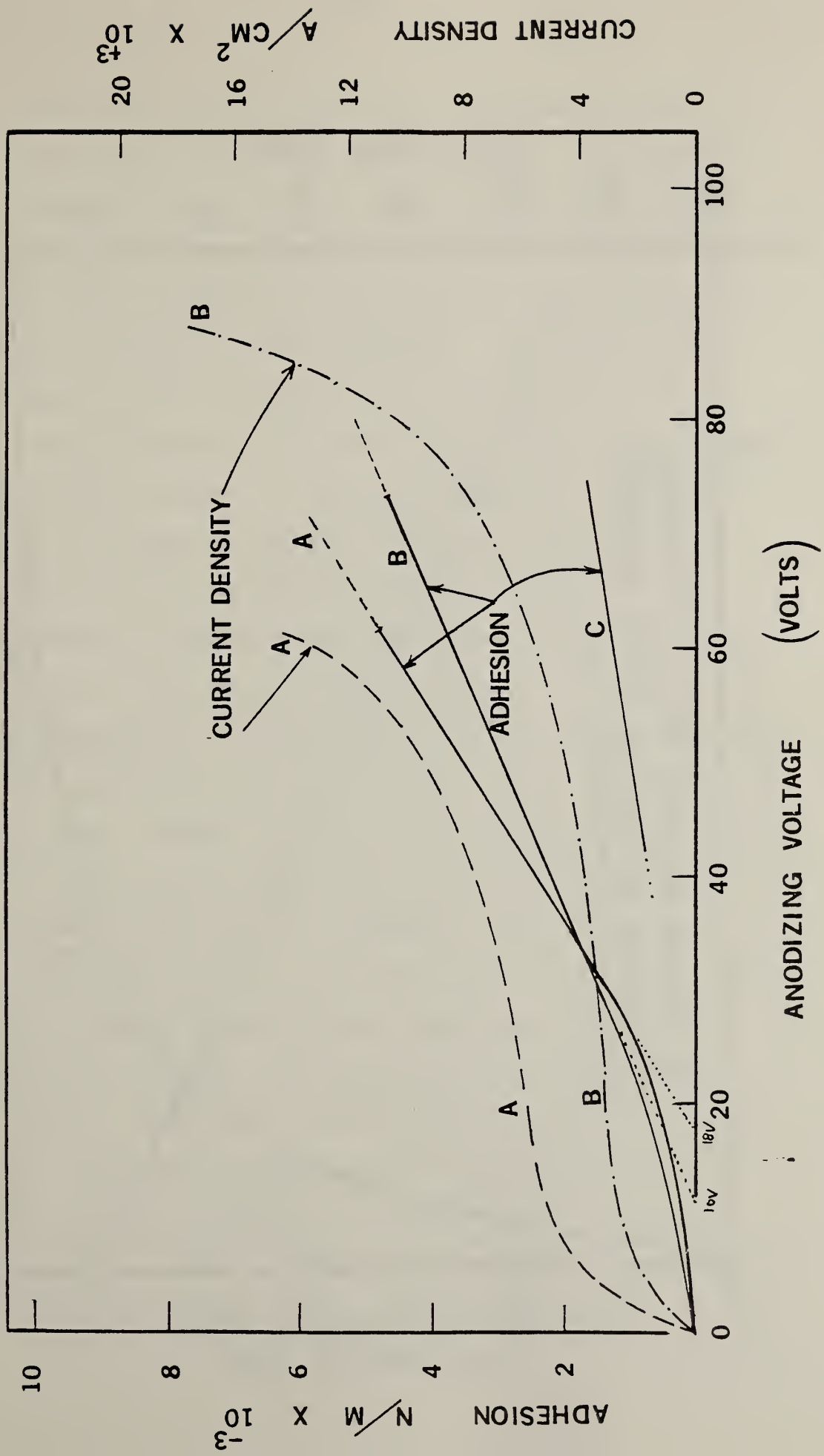


Fig. 1.

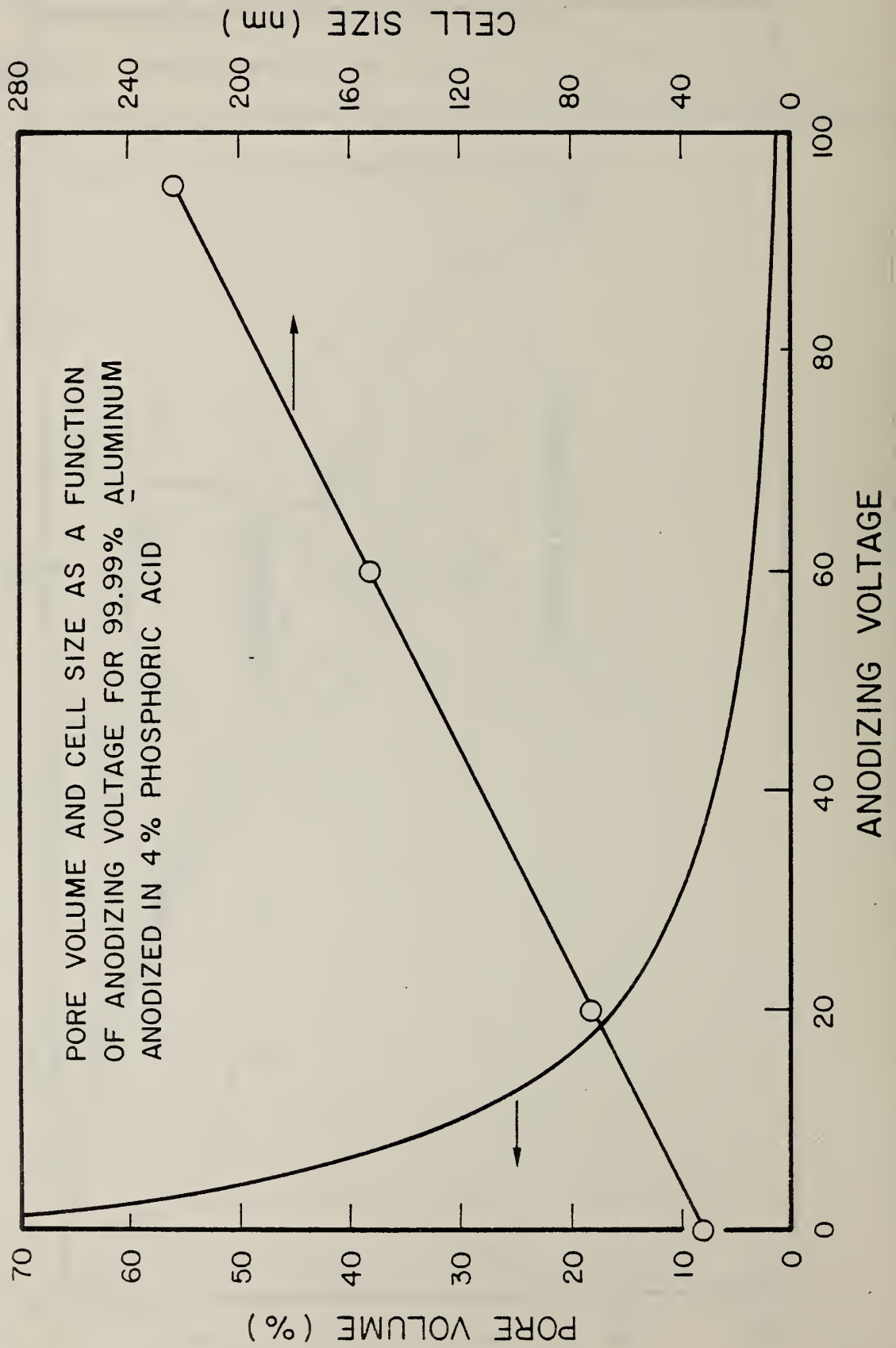
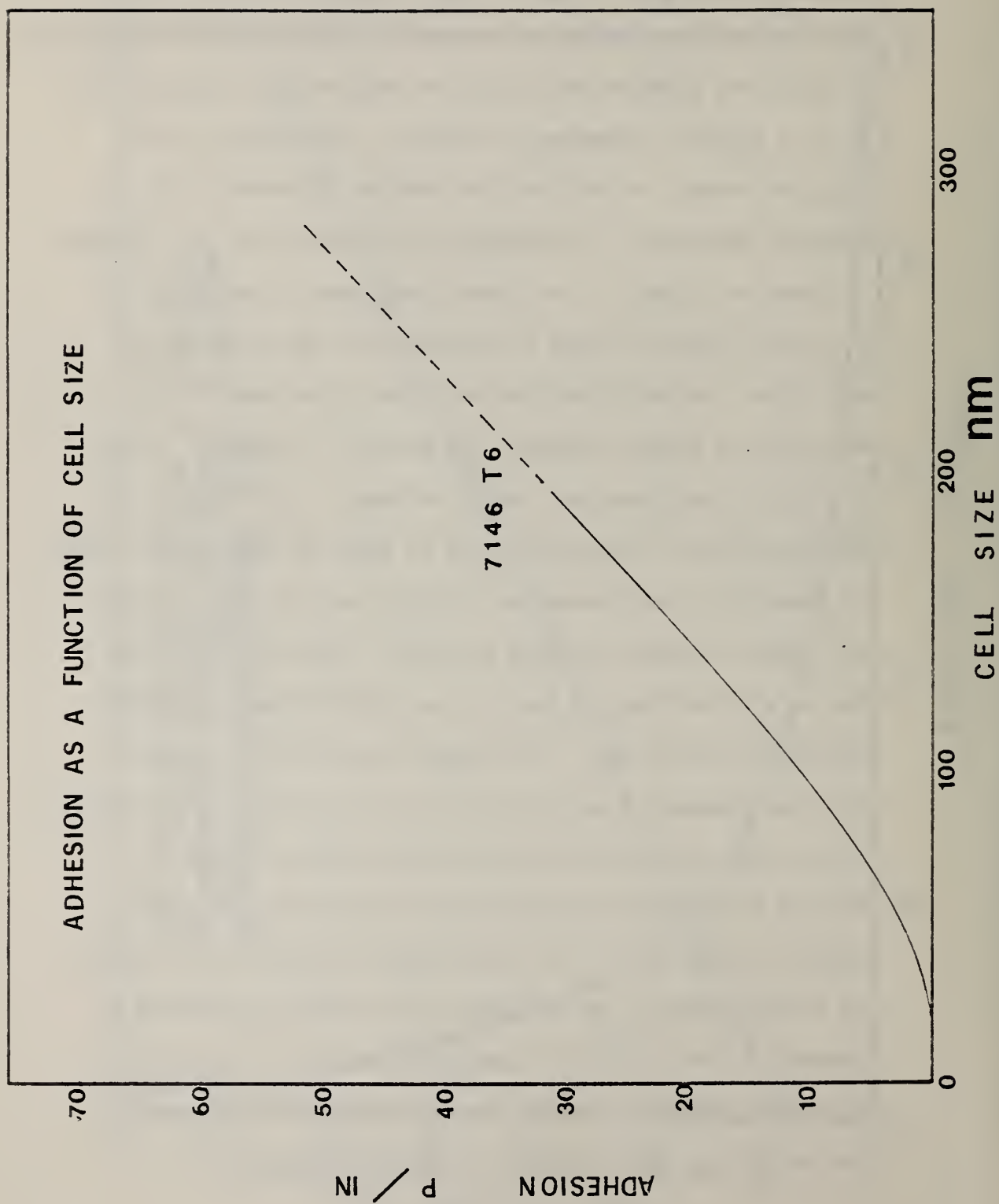


Figure 2. Pore volume and cell size as a function of anodizing voltage for 99.99% aluminum anodized in 4% phosphoric acid.

O'Sullivan and Wood (3) have shown that the pore diameter is also linearly dependent on applied voltage. If the bonding between the pore walls were solely responsible for adhesion, then, as the area available for bonding increased with decreasing voltage, the adhesion would also be expected to increase. The data in figure 2, compared to figure 1, show exactly the opposite trend. As the area for bonding increases, the adhesion decreases. The adhesion as a function of pore diameter is shown in figure 3. The linear dependence of adhesion on cell size shown in figure 2, implies that the oxide is the weak link. As the proportion of oxide in the anodic film decreases at higher voltages, the adhesion increases. This finding is consistent with other evidence. For example, the microstructure of the anodic film as shown by many investigators is essentially the same on all alloys, even on pure aluminum. At higher voltages, as shown by Keller, Hunter and Robinson, the pore microstructure does not vary much between different anodizing electrolytes. For example, oxalic acid, sulfuric acid and phosphoric acid all give rise to similar pore diameters at voltages of around 60 volts, though adhesion variations between alloys and even electrolytes can be more than three orders of magnitude. This new evidence indicates that efforts to improve adhesion of the anodic film should be directed at increasing the strength of the oxide itself. It should be noted that metallic bonding through the base of the pore by the nickel has been ruled out by the TEM evidence.



3.1.2. The Effect of Post Anodizing Treatment:

Extensive experiments on post anodizing treatments have not yet been done. However, preliminary experiments indicate that dilute HF (0.5 vol. percent) solutions provide greater adhesion than the commonly used sulfamic acid. However if more concentrated solutions are used, say 2 g/L, then the adhesion drops off. If the concentration of the sulfamic acid is increased to 4 g/L, then adhesion increases by about 25 percent. The strong HF solutions obviously attacks the oxide, more rapidly than the sulfamic acid.

A possible explanation for the effect of the post anodizing treatment is that the acid removes a weak boundary layer from the pore walls and further cleans out those pores filled with reaction products.

3.2. Microstructure of the Anodic Film:

In order to determine the mechanism of adhesion of nickel, plated in a porous anodic film, a transmission electron microscopy (TEM) investigation of the microstructure was undertaken. Specimens of several different kinds of alloys were investigated and were prepared in either of two ways,: (a) so that the interface was perpendicular to the electron beam, or (b) so that the interface was parallel to the beam. Data from case (b) have not been reported in the literature. Therefore, this investigation represents, the first time that a direct TEM study of nickel plated into the anodic film has been characterized by TEM. The few TEM studies of anodized specimens (not nickel plated) prepared with the interface parallel to the beam were

either of replicas or were of specimens prepared by ultra-microtome techniques.

Anodic film on both 7129-T63 and 7146-T6 were investigated. The specimens were anodized according to Wittrock's procedure. The starting geometry was 10 cm x 10 cm x 0.64 cm (4" x 4" x 1/4") for 7146-T6 and about 5 cm x 15 cm x 0.64 cm (2" x 6" x 1/4") for 7129-T63. The large specimens were used for adhesion determination prior to further preparation. It was thought important to know how an interfacial structure under study was related to a given adhesion value. Following adhesion testing, an untested section near the center of the panel was nickel plated for an extended time in the same sulfamate nickel electrolyte used for peel testing. The plating was continued until 5 mm of nickel was built up.

Foils were then prepared from this specimen so that the interface was perpendicular to the surface — the interface would appear as a line through the foil. Two techniques were used to cut foils: (a) a spark cutter, and (b) a LECO - VARI CUT (VC-50) low speed diamond cut off saw. Foil thickness varied from 75 to 250 μm . The foils prepared by spark cutting were further polished using standard metallographic techniques, with the final polish being 0.01 μm MgO. The diamond cut-off specimens were used without further processing. Both sets of foils were then thinned to electron transparency in an ion - milling machine with 3.5 to 4 KeV Argon ions. This latter technique required milling times in excess of a week, operating 24 hours/day. The thinned foils were then examined in a

Phillips EM 200 A at 100 keV, equipped with the usual anti-contamination stage and a double tilt specimen holder.

3.2.1. A representative micrograph of 7129-T63 anodized in 3 percent phosphoric acid is shown in figure 4. The adhesion, measured by peel testing, exceeded 75 N/m (100 #/in.) The average cell size, at the interface, is about $1250 \text{ \AA}$, yielding a cell density of $6.4 \times 10^9/\text{cm}^2$. The tip radius is about $850 \text{ \AA}$. Several important structural features of the anodic oxide - nickel system are revealed here. First, the nickel has penetrated the pores completely and, secondly, there appears to be a continuous oxide barrier between the nickel and the aluminum. The nickel grain size in this specimen is about $400 - 500 \text{ \AA}$. For this micrograph, the substrate was not oriented for dislocation contrast, so the effect of the aluminum's structure on the growth of the anodic film was not apparent.

The aluminum's structure has a very important effect on the growth of the anodic film, as shown in figure 5. This micrograph was exposed and printed to bring out the dislocation structure. It is seen that, in a number of places, the oxide grows along dislocations. Regions of oxides of $150 \text{ \AA}$ diameter appear to precede the aluminum/oxide interface by as much as $1200 \text{ \AA}$. Moreover, many of the oxide regions appear to have four fold symmetry (though no diffraction from them was observed).

As the ion thinning proceeded into the nickel, it became apparent that the pores (filled with nickel) were not at all uniform, but underwent a great deal of branching, as shown in figure 6 abc. This branching is probably caused by a voltage

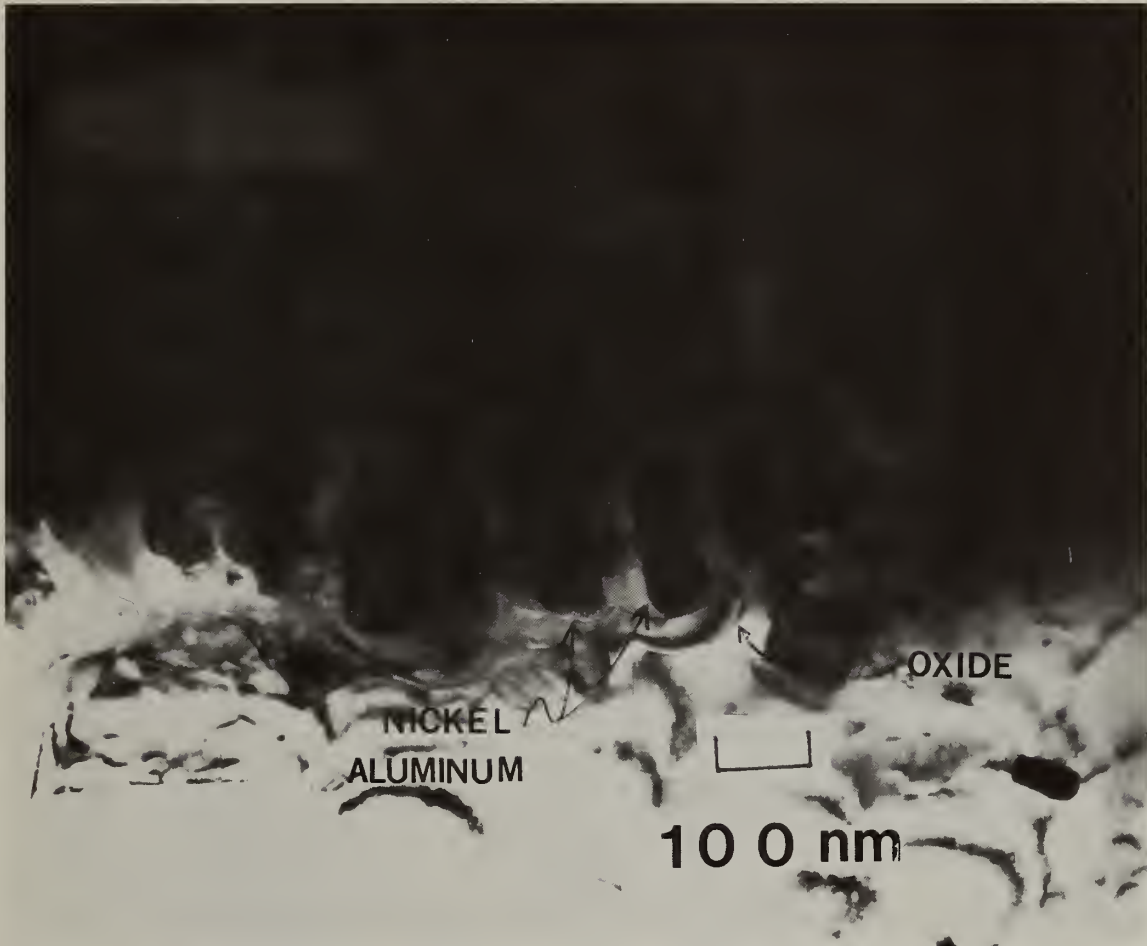
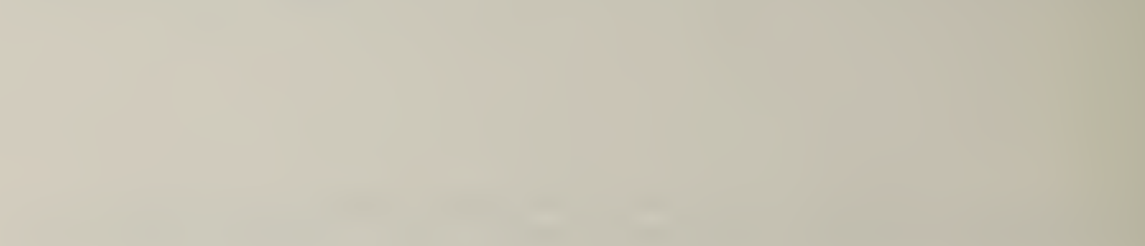
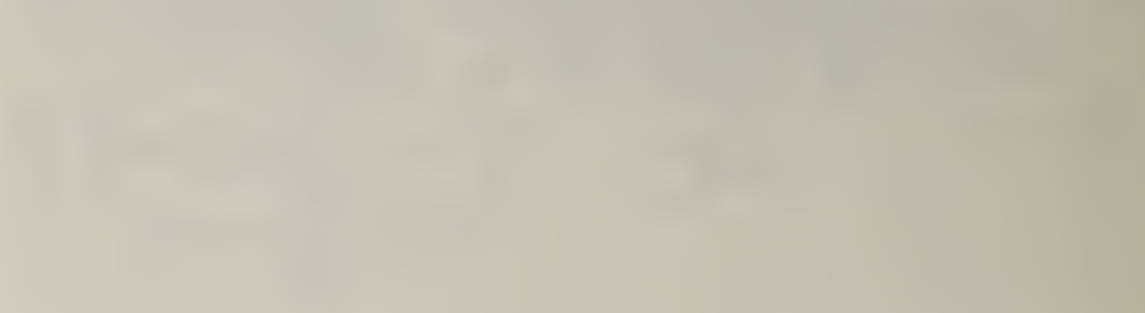
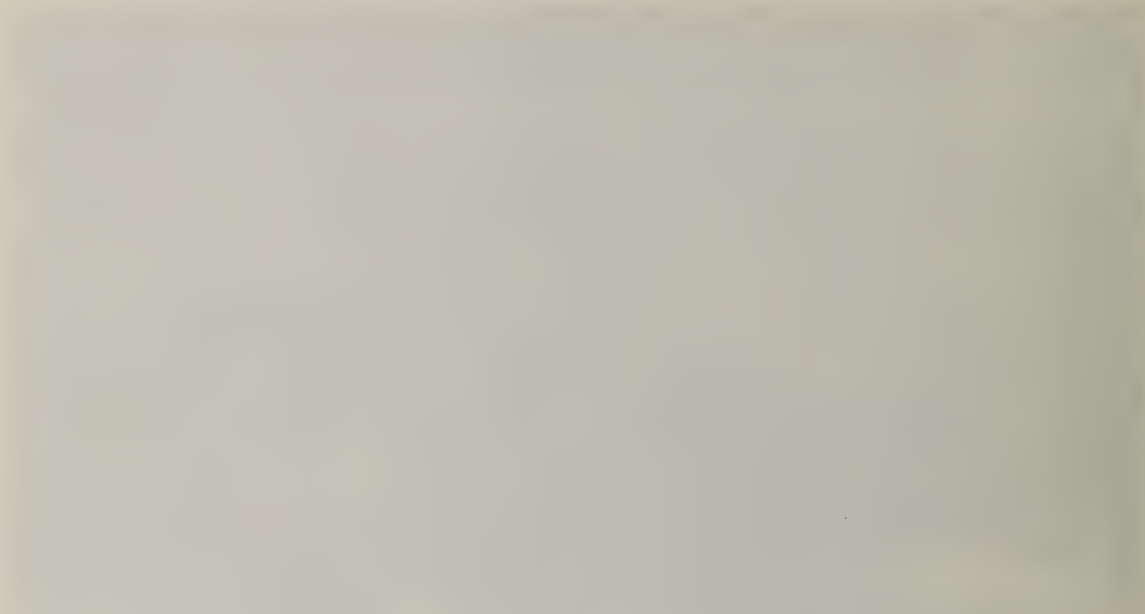


Figure 4. A transmission electron micrograph of 7129 T63 anodized in 3% phosphoric acid then plated with nickel from a sulfamate electrolyte.



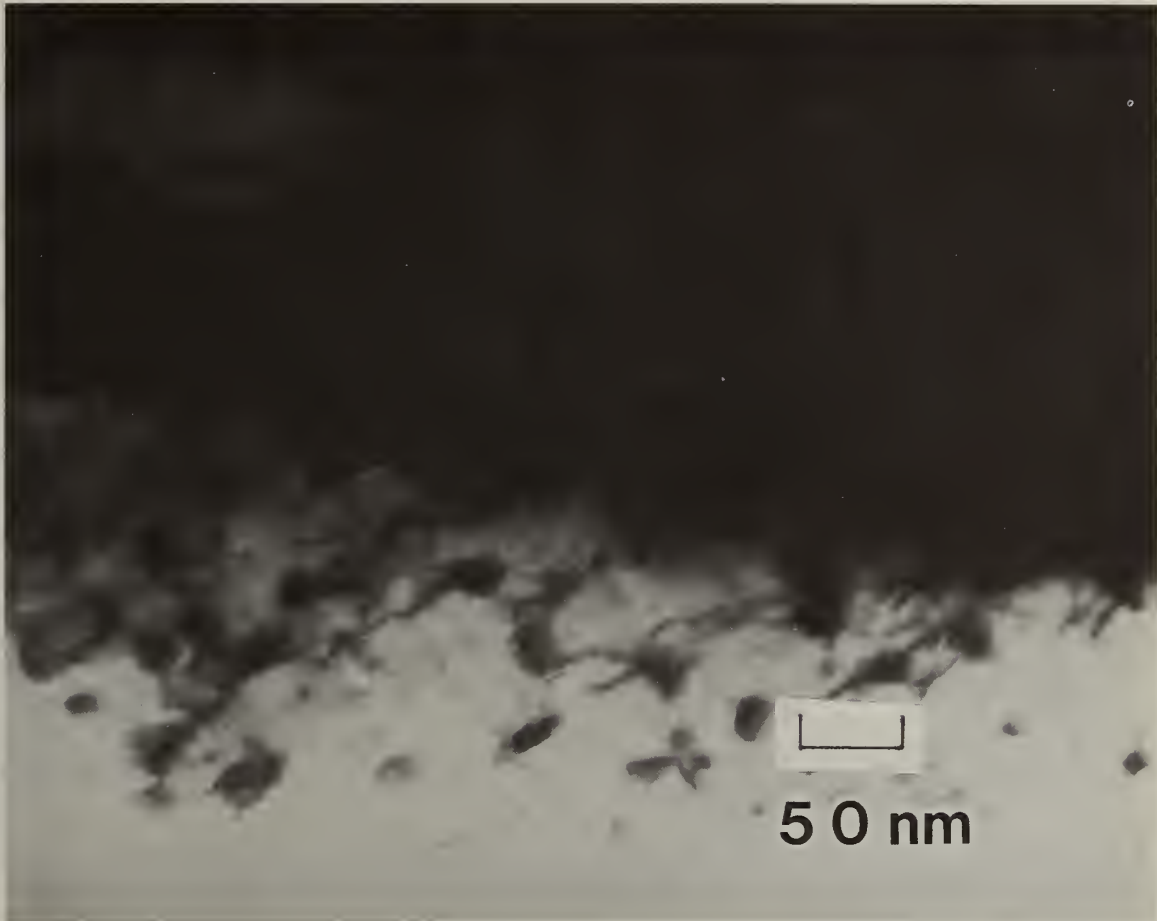
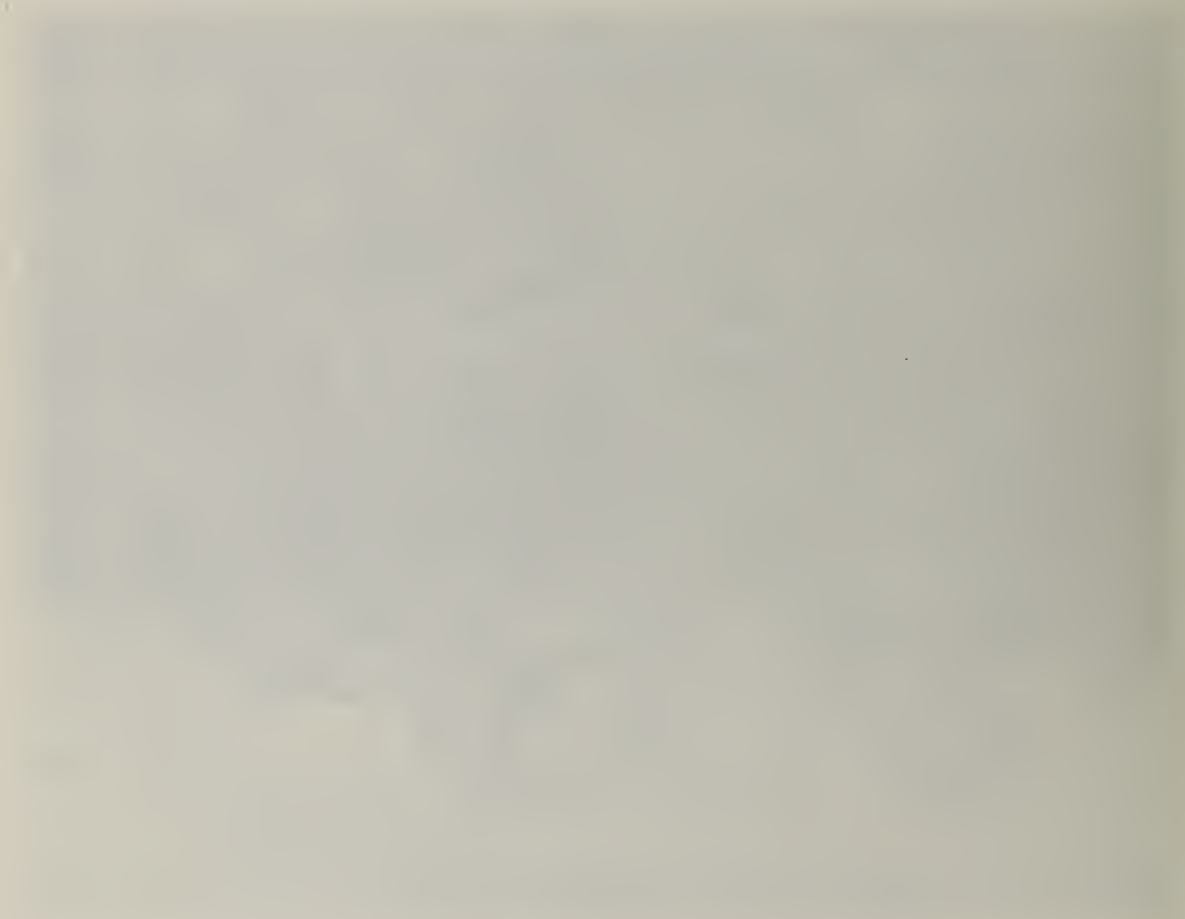


Figure 5. A TEM micrograph of 7129 T63 showing the growth of the anodic oxide along dislocations in advance of the barrier layer. The dark area coresponds to nickel plated into the porous oxide.



Very faint, illegible text or markings at the bottom of the page, possibly a signature or footer.

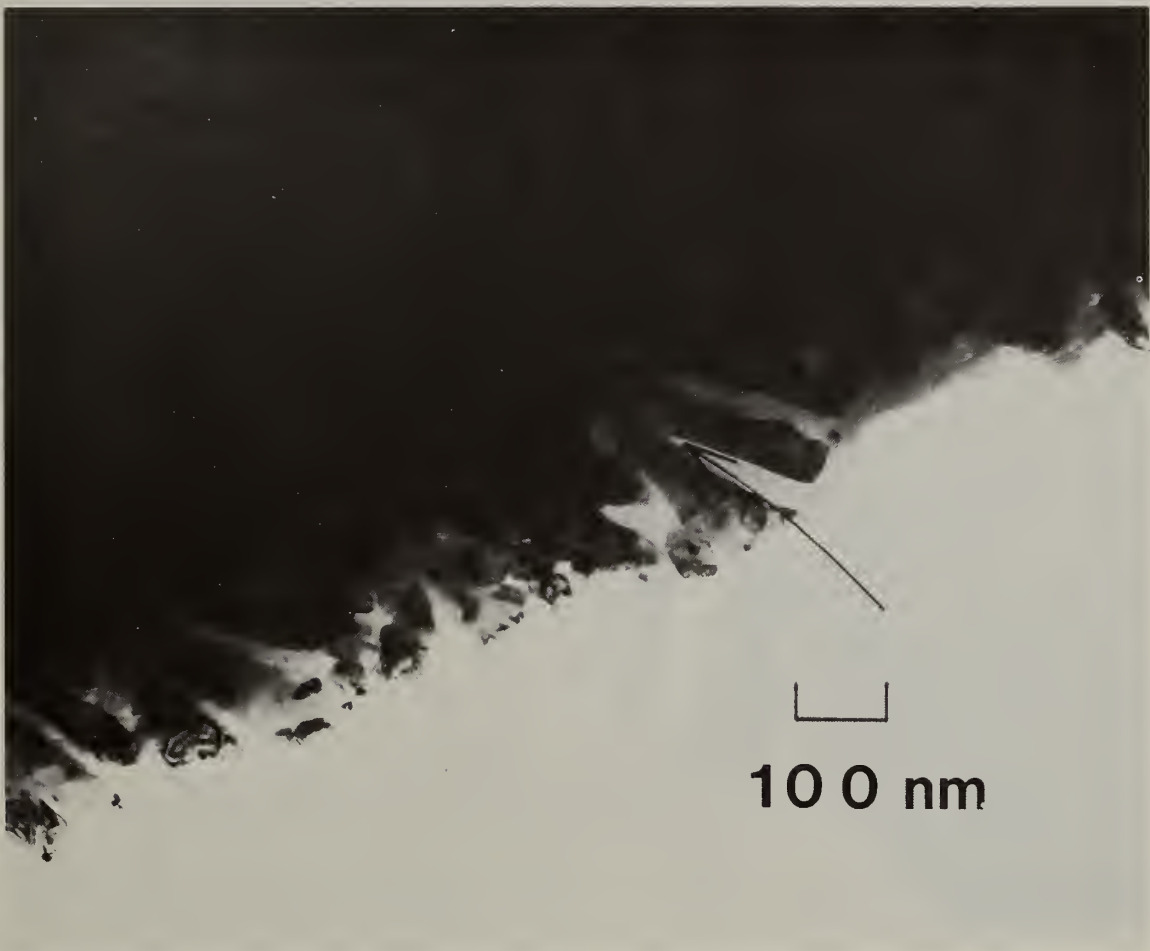
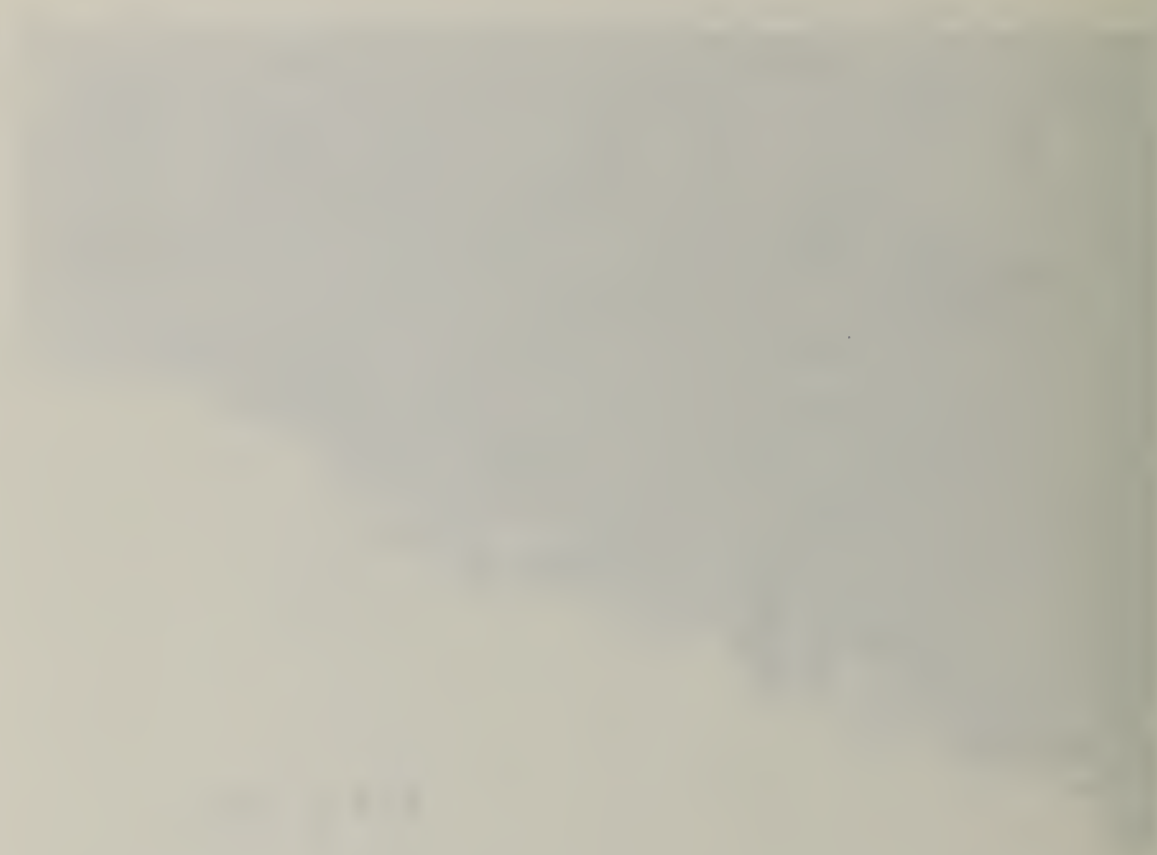


Figure 6a. A low magnification bright field TEM micrograph of nickel plated into a porous anodic oxide exhibiting typical pore branching.



100-1000

100-1000

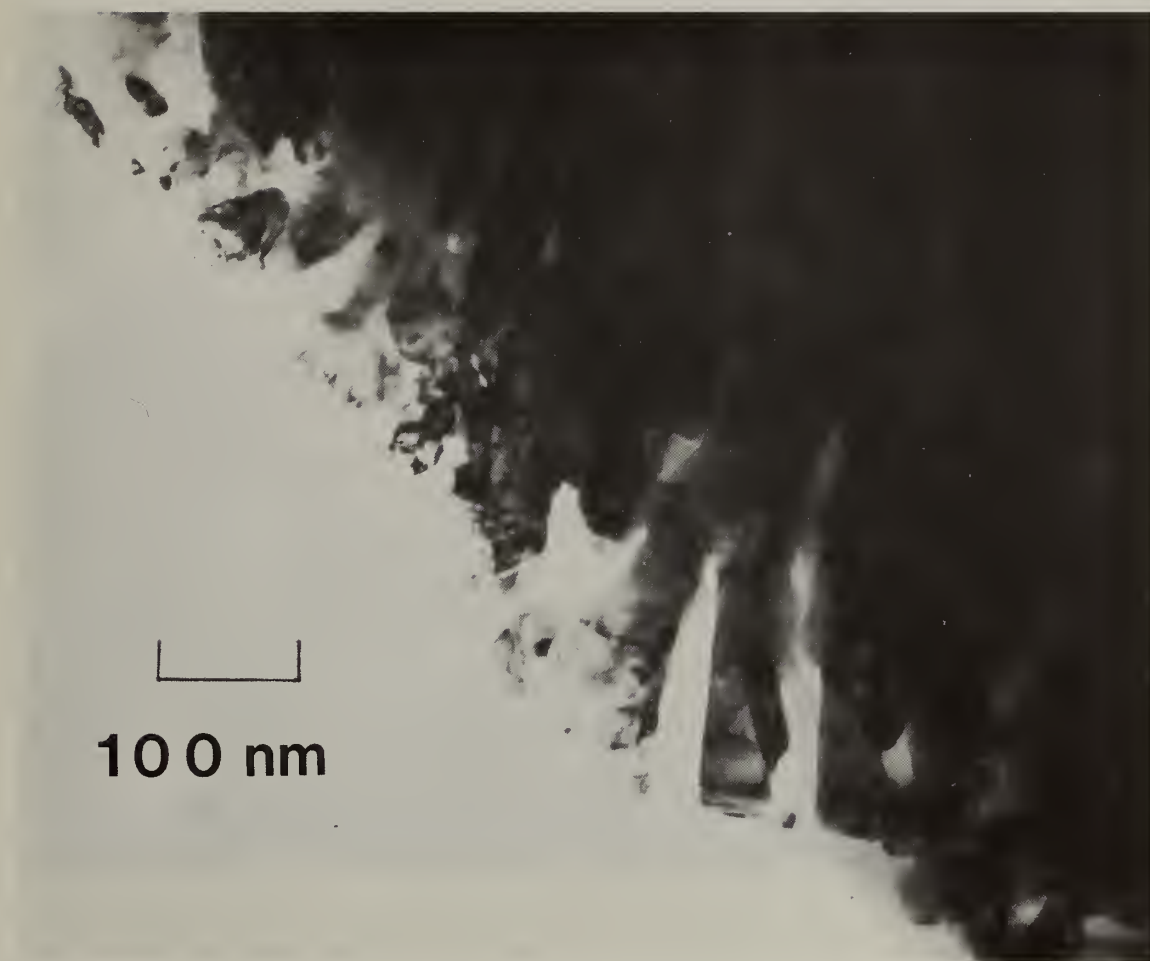
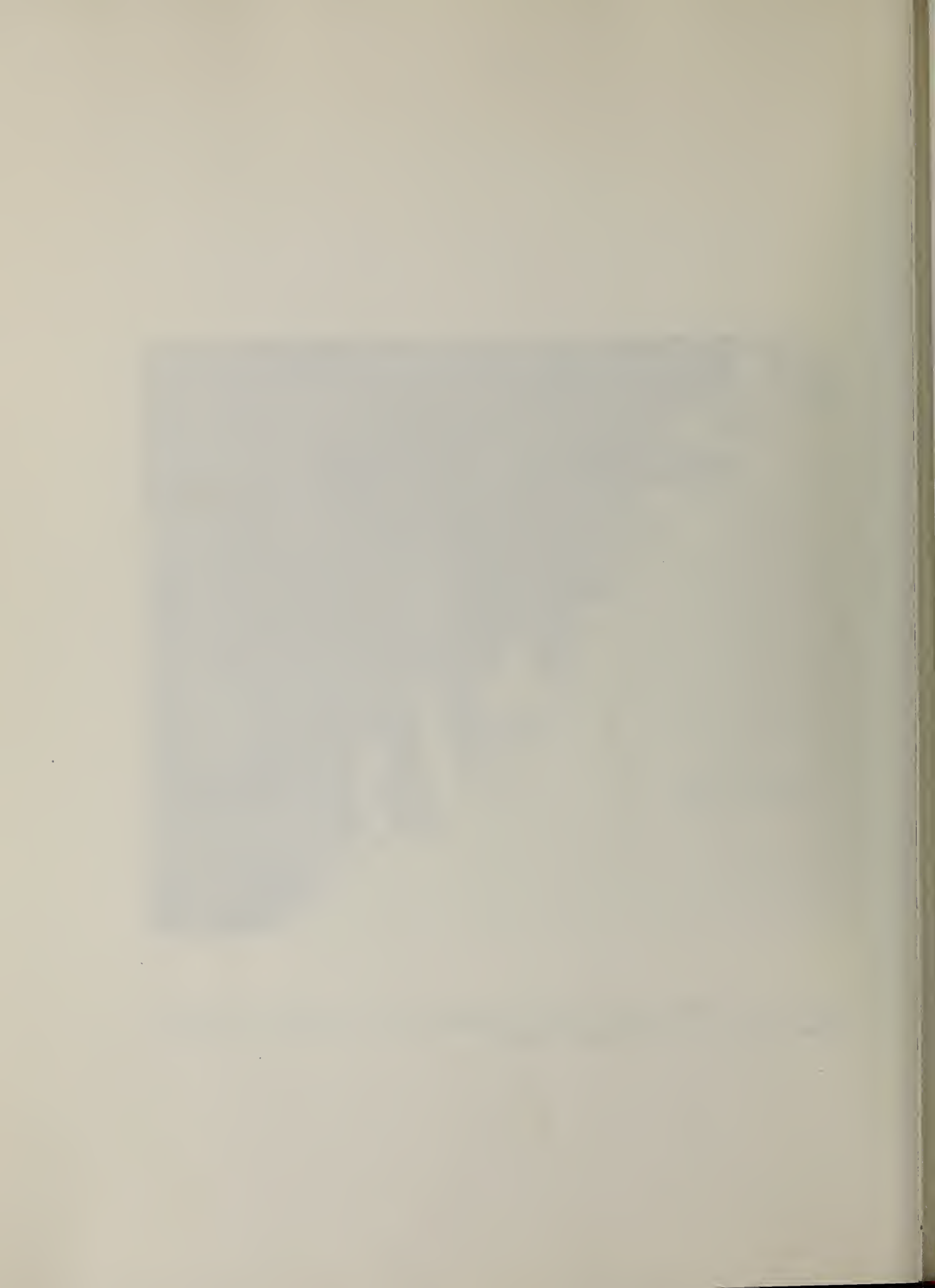


Figure 6b. A TEM bright field micrograph of the same area as shown in figure 6a but at higher magnification.



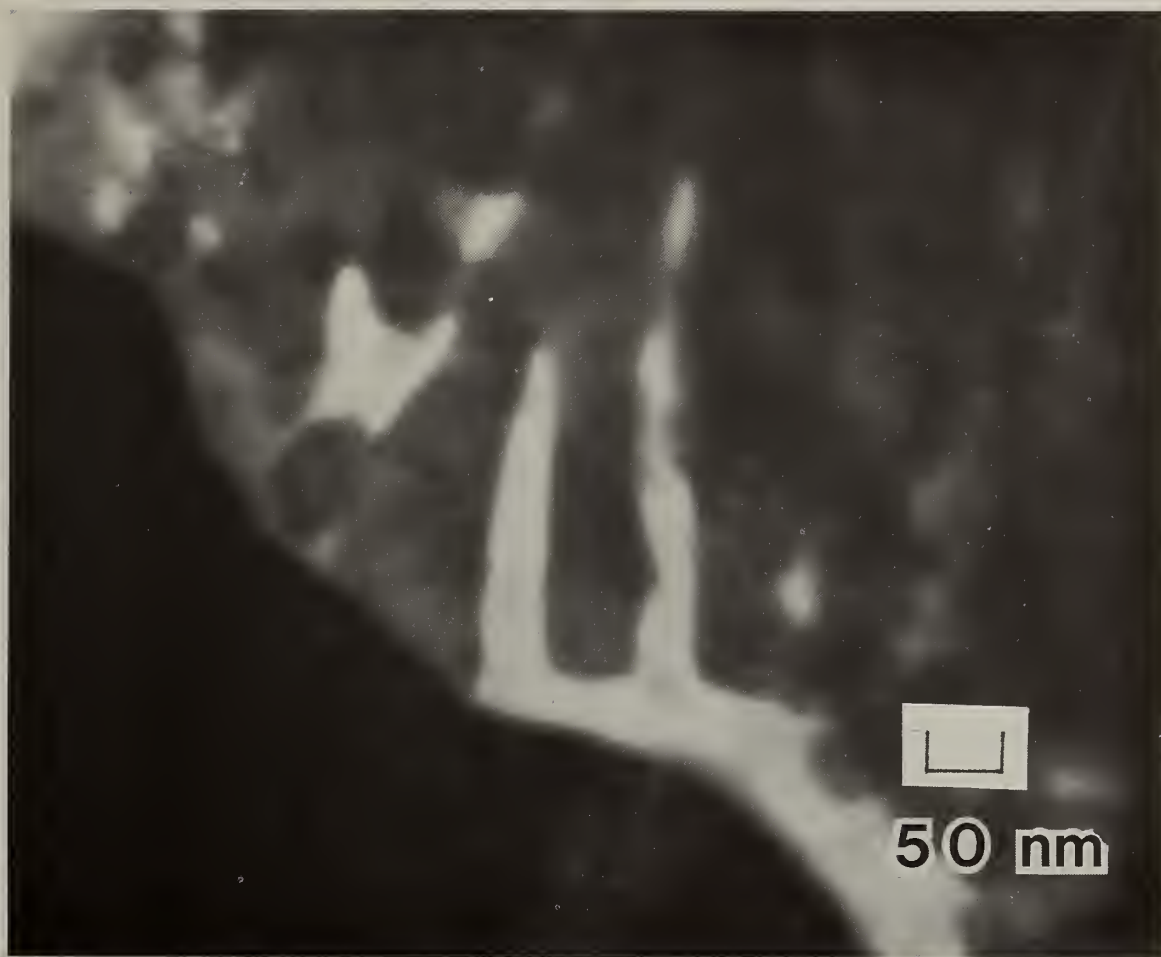


Figure 6c. A Dark field micrograph of the same area as shown in 6a taken with the objective aperature over the diffuse oxide ring.



transient at the initial stages of film growth. Certainly this type of microstructure would result in a strong mechanical bonding.

3.2.2. The initial stages of growth of the anodic film on specimens of 7146-T6 were studied by TEM, with the beam perpendicular to the interface. The mechanism of initial film formation is apparently different from growth at a latter stage. Several surprising results were observed in figure 7. A large number of rectangular and even square regions of oxide are observed on the (100) plane of 7146-T6. This observation indicates that a strong role is played by the structure of the substrate. These regions of oxide grow in such a way as to form pores, as indicated on the micrograph. Even the large pores show evidence of being made up of rectangular 'building blocks' of oxide. The second major feature observed during the initial stage of film formation is a large number of fringes which may be Moiré fringes. If subsequent study shows this to be the case, then it is clear that the oxide forms, at least at the initial stage, an epitaxial (or perhaps pseudomorphic) layer before becoming amorphous. No evidence of crystalline oxide was detected in the diffraction patterns.

The white areas shown in figure 7 are etch pits. The classical model of pore growth requires field assisted dissolution at places where the oxide is weakest and this model is supported by the evidence in Figure 4. However, in the initial stages of oxide formation, the weak areas are not necessarily associated

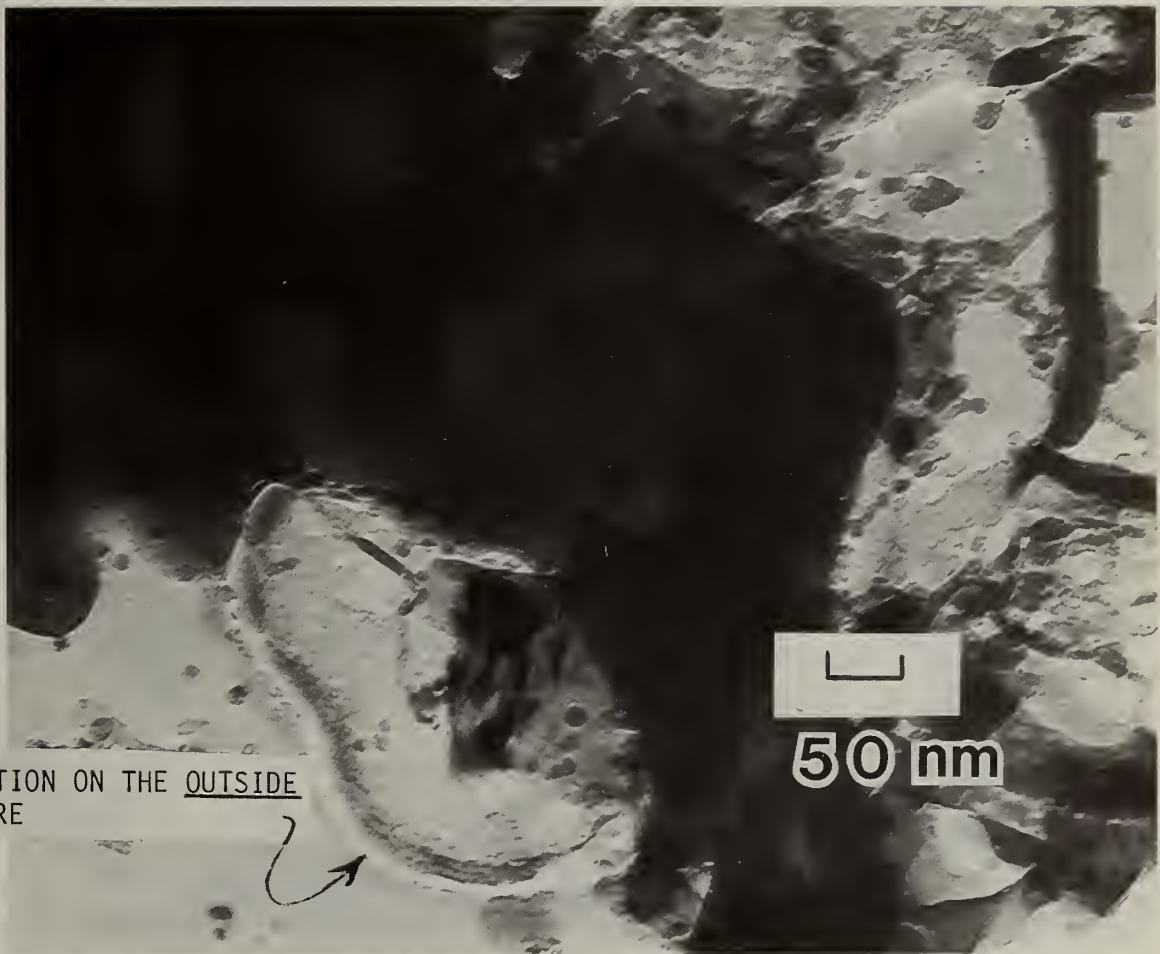


Figure 7. A TEM micrograph of the initial stages of anodic film formation on 7146 T6. The electron beam is now perpendicular to the interface. Note that the surface is covered with Moire fringes which may indicate an epitaxial oxide forms during the initial stages of anodization.

with pores or even regions of oxide thickening. Indeed, the oxide growth is remote from the dissolution sites. Some pores contain only a few dissolution sites and some none at all. Thus, initially the film formation mechanism can be quite different from latter stages. Further evidence for this is shown in figure 8, where aluminum dissolution is observed to occur on the outside of a large pore. In this figure, a number of well developed pores are also observed to have no evidence of dissolution at their base; just the opposite, the base of the pores seems to be filling in with oxide. It is thought, however, that once the surface is covered uniformly with oxide, the oxide will redissolve within the pore base. Very large crystallographic regions of oxide are apparent in this micrograph.

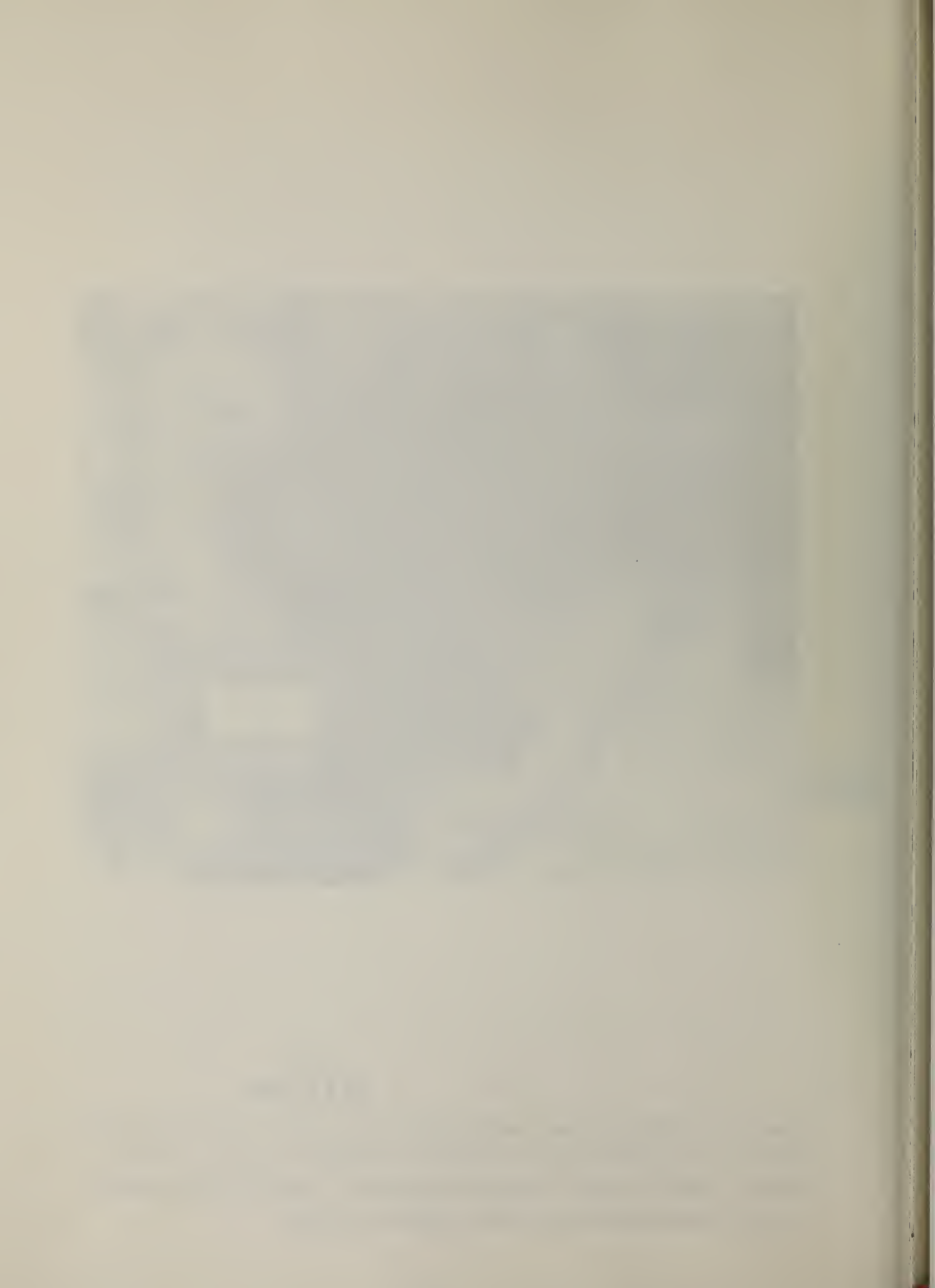
At a latter stage of growth, as shown in figure 9, the pores take a more classical appearance. However, note that both the inside and outside of the pore walls have a structure distinct from the interior material. It is thought that the interior material is removed during the post anodizing treatment.

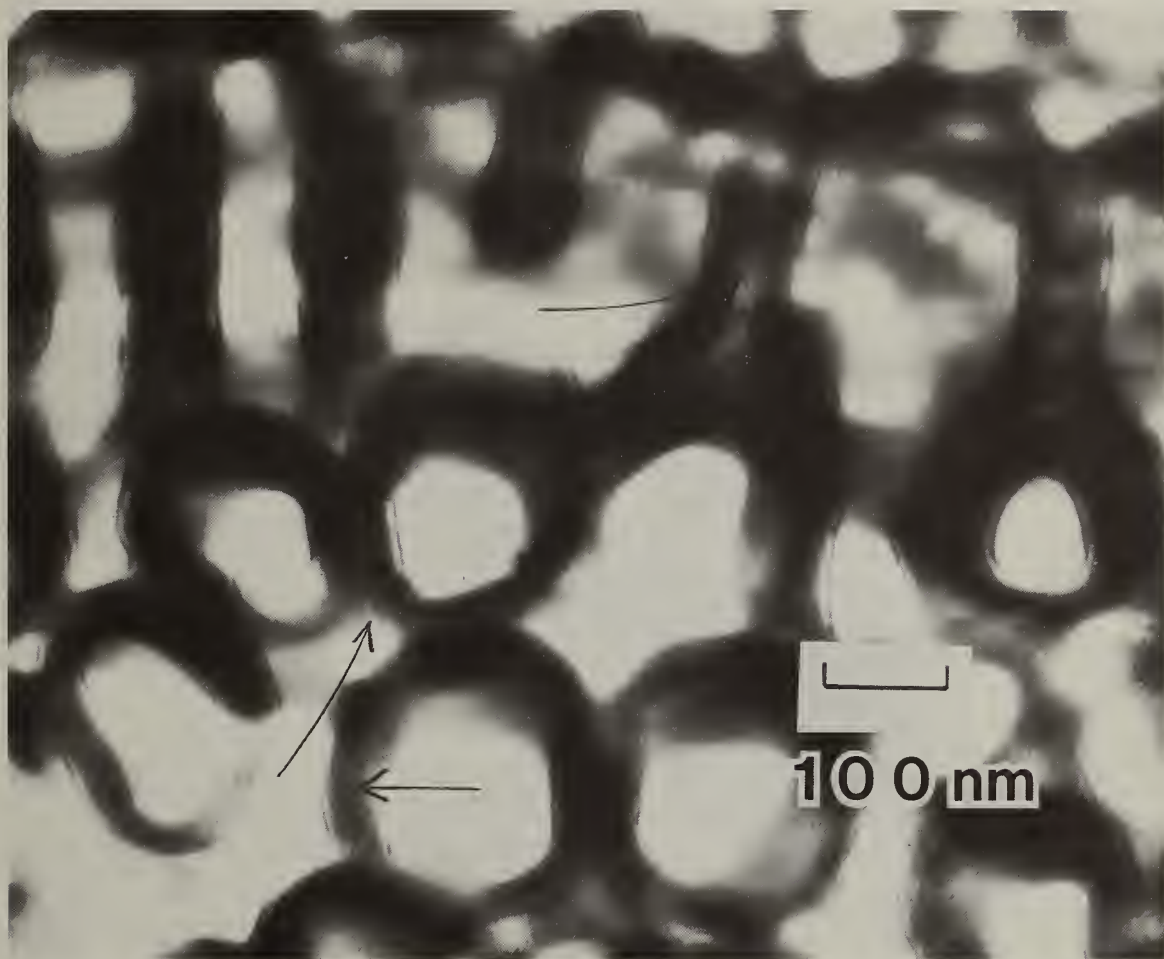
The microstructure of the equilibrium oxide structure oxide is presented in figure 10. The small pore diameter present at the initial stage of growth gives way to a pore diameter characteristic of the applied potential and dissolution now takes place through the base of the pore. This is shown in this dark field micrograph as a black area in the pore center. The observations made above are shown schematically in figure 11.



50 nm

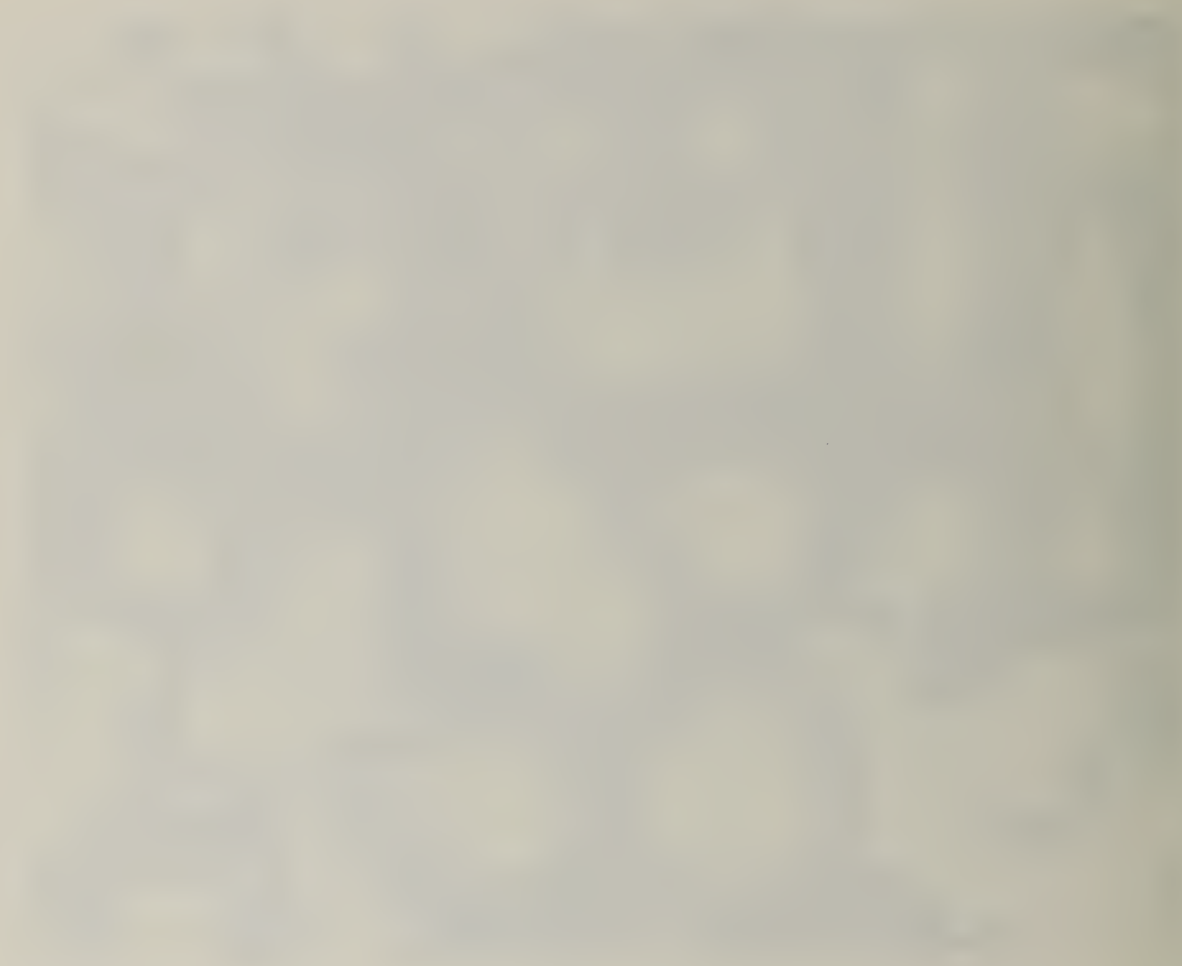
Figure 8. A TEM micrograph showing dissolution of the aluminum around the outside of an established pre rather than through its center as in the classical model of Keller, Hunter and Robinson. Note that this behavior is only observed during the initial stages of growth.





100 nm

Figure 9. A TEM micrograph of a latter stage of film formation on 7129 T63 indicating the existence of a substructure to the cell walls.



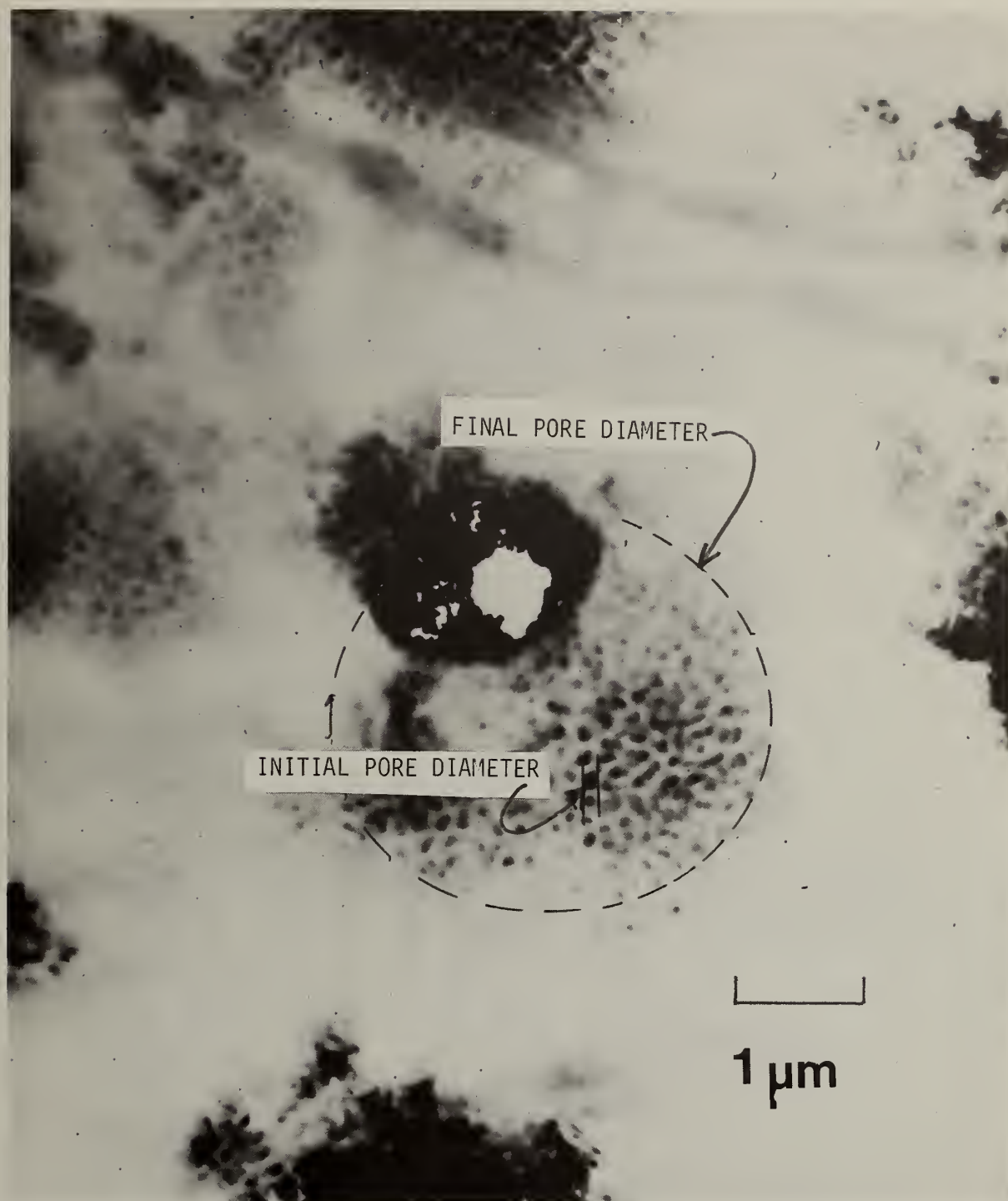


Figure 10. A TEM micrograph showing the transition from the large numbers of small pores formed initially to the large diameter equilibrium pore geometry.





Figure 11. A schematic diagram of pore formation on 7000 series alloys: the initial stage.

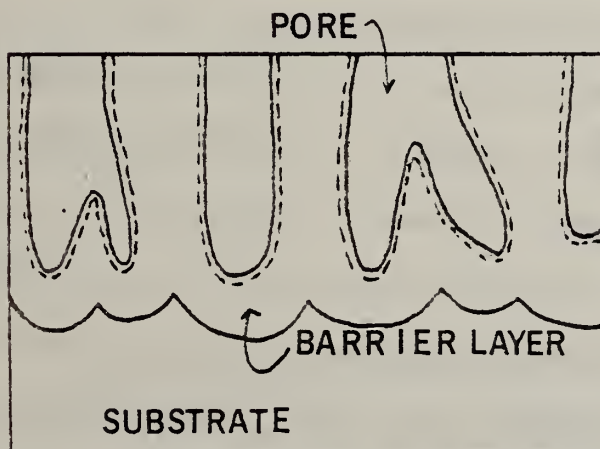


Figure 12. A schematic diagram of a mature pore structure on 7000 series alloys. (these models are probably not alloy dependent).

At a latter stage of growth the structure of the pore wall seems to change, as does the location of the place in the substrate where dissolution occurs. A schematic diagram of a mature pore (cell) structure is shown in figure 12.

3.3. Electrochemical Measurements:

Three representative alloys 7129-T63, 7146-T6, and 99.99 percent aluminum were investigated to determine if observed differences in their electrochemical behavior could be correlated with their subsequent adhesion performance.

3.3.1. Current Density versus Voltage Data:

Current density as a function of anodizing voltage curves are shown in figure 1. From this data, there appears to be three distinct regimes of growth, marked accordingly in the figure. Region one, extending from about 0 to 10 volts, approximates Ohms Law ($V = IR$), with a low surface resistance of from 1 to 2 Ω/cm^2 . In region two, this resistance increases with increasing voltage to a maximum of around 500 Ω/cm^2 ; in region three, the resistance becomes small. Clearly, in region three a dominance of the dissolution process over the film formation process is apparent. In region one, the surface is relatively free from large amounts of oxide and, in this unprotected state, is relatively conductive, so its resistance is low. Film formation and growth takes place in region two. As the temperature increases, the rate of film formation increases, along with the rate of film dissolution. In order to further examine the initial stages of growth, scanning voltammograms of the regions between 0 and 10 volts were made.

3.3.2. Scanning Voltammetry:

Specimens of 1 cm^2 area were prepared for these measurements in the following way. Each was metallurgically polished with the final step being $0.01 \text{ } \mu\text{m}$ MgO. This technique yielded reproducible measurements which were comparable to those obtained on electropolished specimens. Simpler grinding techniques yielded spurious data. Results for 99.99 percent aluminum, 7146-T6 and 7021-T63 are shown in Figure 13. Each set of curves corresponds to three successive measurements starting with a freshly polished surface and zero volts, then sweeping the potential to 10 volts (limited by our apparatus), then restarting the sweep. Data from figure 13 is reproduced in Table I.

Table I: Scanning Voltammetry Data.

Alloy	99.99 percent Al	7146-T6	7021-T63
Break pt. on 1st Sweep	3.1 V/SCE	3.5	2.3
Break on all successive sweeps	2 V/SCE	21.9	
Resistance before 1st break in curve	$50 \text{ } \Omega/\text{cm}^2$	37	54
Resistance (steady state)	$18 \text{ } \Omega/\text{cm}^2$	20	18

During the first three volts, the resistance is markedly higher than during the higher voltage regions. This observation implies a lack of significant porous film formation below potentials of three volts/SCE and, probably, pore formation does not start until the first break point, though this

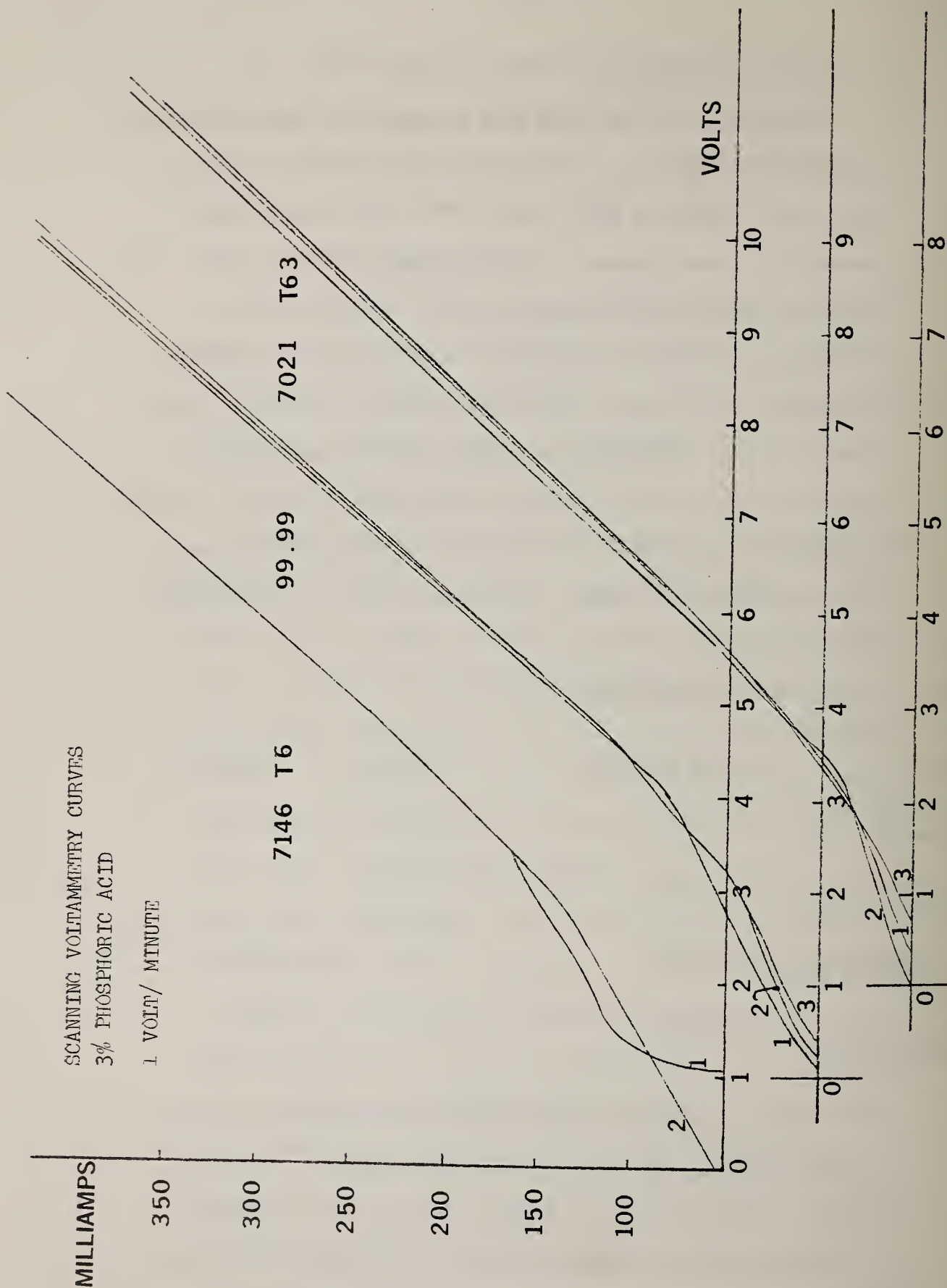


Figure 13. Scanning voltammetry curves for
phosphoric acid anodized (a) 7146 T6
(b) 99.99 (c) 7021 T63

has not yet been confirmed. Clearly, there is a reproducible difference in alloy behavior. It would appear that pore formation in 7021-T63 and in pure aluminum must have similar forming rates and, probably, similar morphologies, though this also has not yet been confirmed. This data was obtained in three percent phosphoric acid electrolytes at a temperature of 60 °C.

References

1. Ya. I. Aleksandrov, Soviet Electrochemistry, 15, 2(1979) 141
SEOCAI (2), 137-244 (1979) in English.
2. F. Keller, M. S. Hunter and D. L. Robinson, J. Electrochem. Soc.
411, (1953).
3. J. P. O'Sullivan and G. P. Wood, Proc. Royal Soc. London A. 317,
(1970)511.

IV. Immersion Deposition:

Many of the results of the characterization of the immersion deposition process have been published in previous progress reports and in appropriate journals and will not be discussed again here. Some results, however, have not been published. These are the product of scanning voltammetry and simple dissolution experiments of zinc films in various acids.

4.1. Scanning Voltammetry:

Specimens of 99.99 percent aluminum were metallographically polished, with the last step being $0.01\text{ }\mu\text{m}$ MgO. The specimen surface area was 1 cm^2 . The voltammetry experiments were conducted by switching on the potentiostat just after the specimen was inserted into the electrolyte. The voltage was swept at a rate of 1 volt/minute to about -2.1 V. Three or four specimens were run for each set of parameters to insure that the data presented below is representative.

In Figure 14a, the curves for the ASTM I electrolyte (calomel reference electrode) are presented. The H_2 peak appeared only on the reverse sweep. The single dip in the curve was characteristic of this electrolyte and may be due to a reduction of the $\text{Zn}(\text{OH})^-$ ion to zinc. The voltages shown with arrows are with respect to the hydrogen electrode.

The results of adding ferric chloride and Rochelle salt to the electrolyte of Figure 14a are shown in Figure 14b. The original dip in the curve observed in Figure 14a is still present, however, with at least three more perturbations apparent. The first, occurring at about 1.44 V(SCE), may be

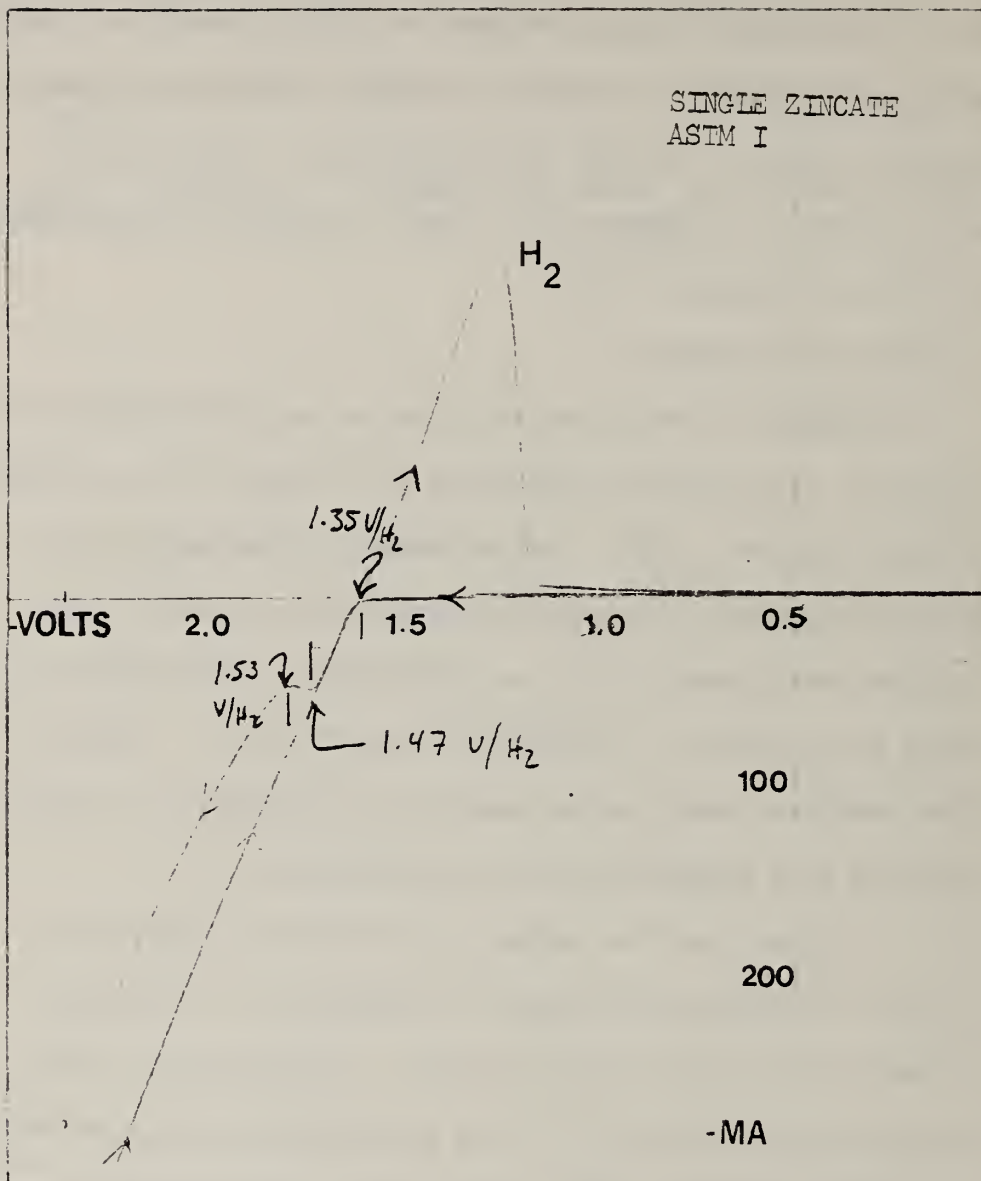


Figure 14a. Scanning voltammetry curves for the ASTM I zincate electrolyte 99.99% aluminum.

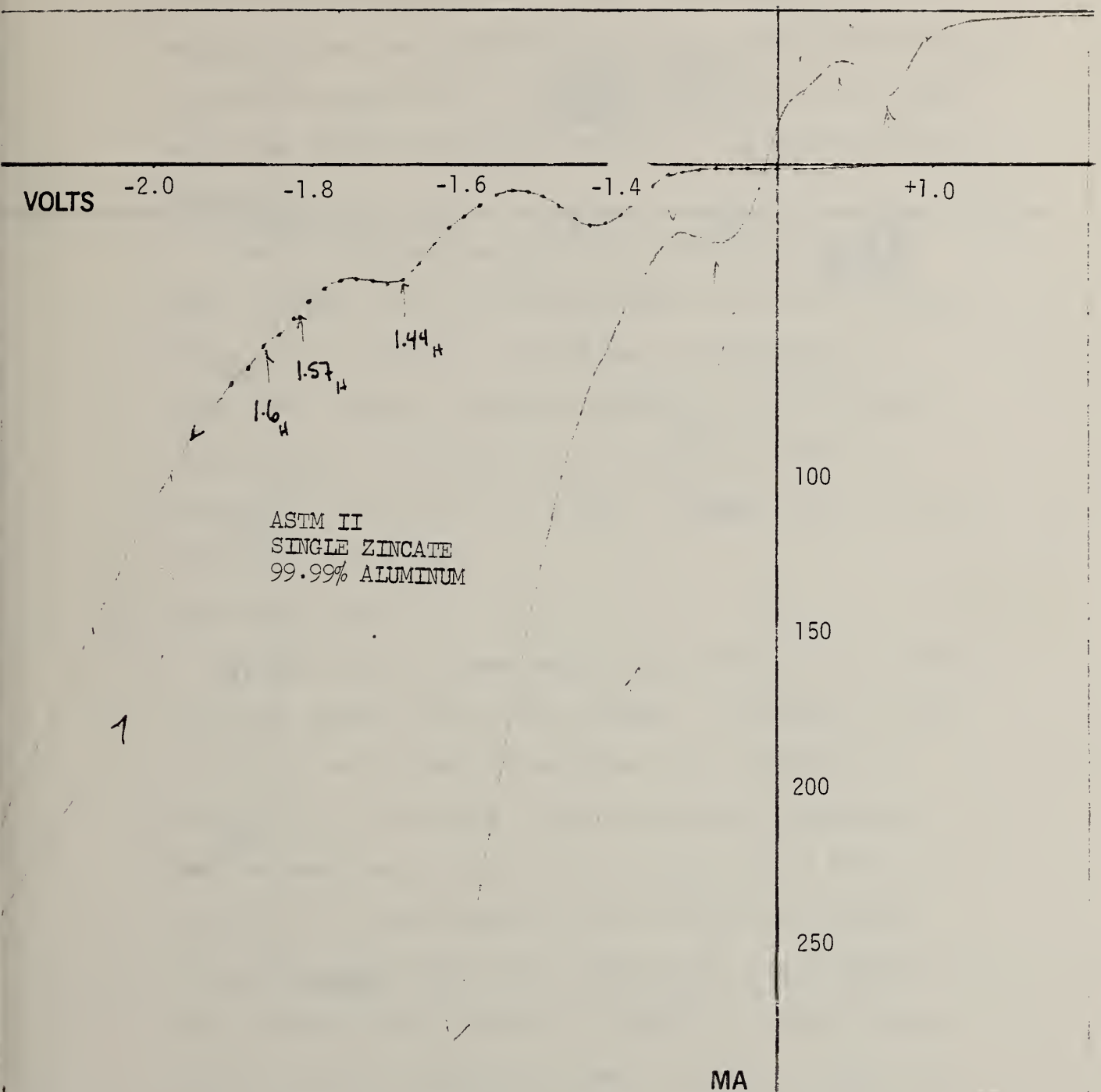


Figure 14b. Scanning voltammetry curves for ASTM II zincate electrolyte. This is the same electrolyte as in 14a with the addition of ferric chloride and Rochelle salt.

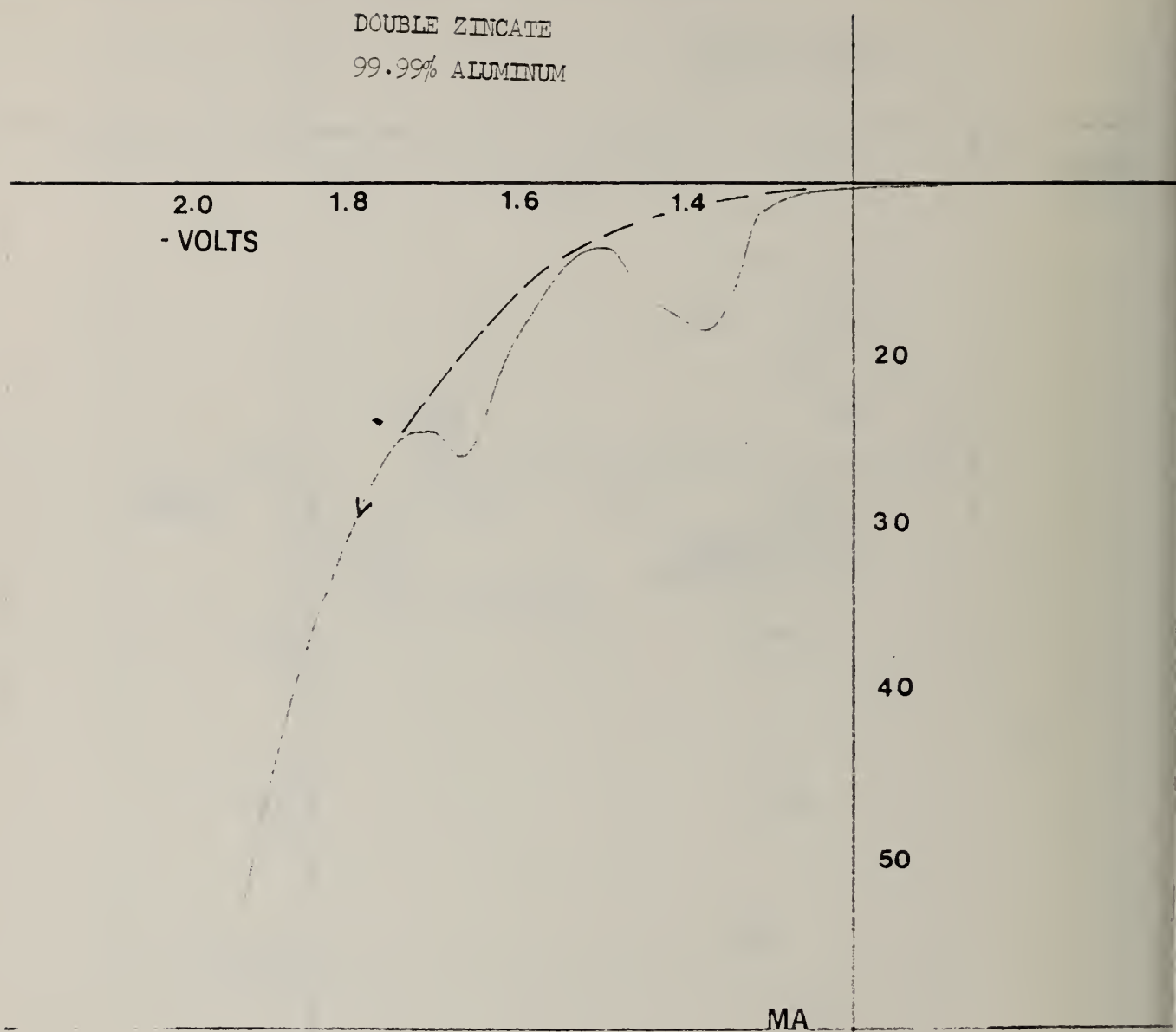


Figure 14c. Scanning voltammetry data for the double zincate procedure with the same electrolyte as in 14b. This data represents the second zinc immersion.

due to a reduction of Fe(OH)_2^- and implies that the iron would be deposited before the zinc. This is consistent with results reported in previous progress reports and by other investigators. The reactions which occur at voltages greater than 1.8 V (SCE) may be due to the reductions of iron-zinc, and Rochelle-zinc, complexes.

The data obtained for the double zincate procedure are shown in Figure 14c, and closely resemble the results from the single zincate procedure from the same electrolyte; i.e. figure 14b. The main difference observed is in the shape of the first peak. Instead of occurring at 1.44 V(SCE), as in figure 14b, it occurs at 1.37 V(SCE). Another peak is clearly observed at 1.44 V(SCE).

4.2. Dissolution Data:

A large number of experiments were conducted in an attempt to further improve the zincate procedure. Specimens of about 12 cm^2 area were buffed and degreased, etch cleaned, and desmutted, as in the normal zincate pretreatment procedure. Most specimens were immersed for one minute in the ASTM III electrolyte at room temperature unless otherwise indicated. The specimens were then placed into various acid solutions and their potential with respect to a calomel or nickel electrode was monitored as a function of time. A typical voltage-time curve is shown in figure 15. In most cases, three or four distinct regions of dissolution are observed. The first part of the curve, region I, is believed to correspond to dissolution

Table I: Summary of Dissolution Data.

Alloy	Acid	Regions			Remarks
		I sec.	II sec.	III sec.	
6061-T6	5% H_2SO_4 , 25 °C	14	13	22	Figure 2 a, ref. Ni.
7129-T63	5% H_2SO_4 , 25 °C	3	15	31	Figure 26, ref. calomel Zincate at 40 °C.
1100	1% H_2SO_4	~12	16	22	Single Zincate, Figure 2 c
1100	1% H_2SO_4	8	8	23	Double Zincate, Figure 2 d
1100	1/2% H_2SO_4	17	23	45	Single Zincate, Figure 2 e
1100	5% H_2SO_4	6	8	12	Figure 2 f
1100	10% H_2SO_4	2	2	4	Figure 2 g
6061-T6	5% H_2SO_4	~6	6	11	Figure 2 h, ref. Ni.
7146-T6		←	12	→ 21	
7146-T6	1/2% H_2SO_4	8	7	36	Figure 2 i
	1/4% H_2SO_4	18	8	>40	
7146-T6	3% H_2SO_4	← 9 →		20	Figure 2 j, 3 min. in zincate
	5% H_2SO_4	← 21 →			
7146-T6	5% H_2SO_4	5	7	26	Double Zincate 2 k

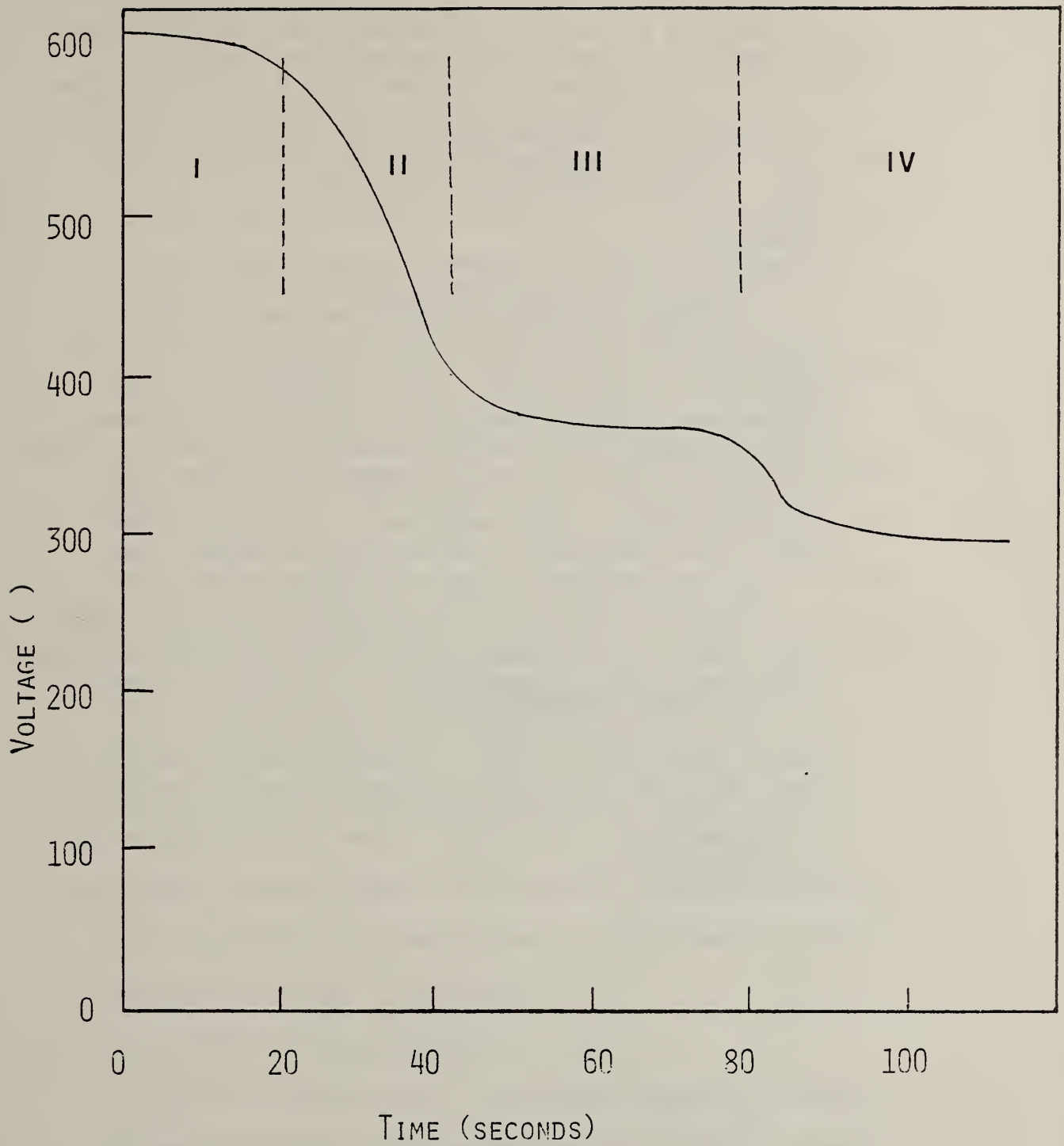


FIGURE 15. A TYPICAL DISSOLUTION CURVE OF ZINCATED ALUMINUM

of the bulk zinc crystallites, and region II to correspond to a dissolution of the initial zinc layer (see progress reports III & IV). The rather long plateau, region III, is believed to correspond to the dissolution of an iron-zinc, or iron alloy. The data are summarized in Table I.

4.3. Discussion:

The double zincate procedure results in an increase in the dissolution time of Region III which corresponds to the dissolution of an iron-zinc alloy. Therefore, the double zincate procedure is believed to result in enhancement of the iron alloy coating. This speculation is supported by the shape of the first peak in the scanning voltammetry data.

Using this dissolution data, specimens were transferred after Stage I to a sulfamate nickel electrolyte and were found to form adherent electrodeposits, as was discussed in an interim report August 1979. This process avoids the use of a cyanide copper strike but is essentially equivalent to the ALCOA 661 process.

V. Adhesion Theory

5.1. Adhesion of Metallic Coatings:

Whenever two clean metals are placed in intimate contact, strong adhesive bonding occurs as was shown by Buckley (1). A theory discussing this type of bond was presented by Ferrante and Smith (2). Although the theory of Ferrante and Smith was based on first principles, neither the effect of interfacial dislocations nor the effect of stored strain energy was included in their calculations. Several mechanistic theories that have been published in the literature include the weak boundary layer theory of Bickerman (3) and a Griffith-Irwin type theory presented by Good (4) and others (5-9). An understanding of the forces responsible for bonding are important, not only for electrodeposited coatings, but also for the fields of friction, wear, and fracture. The development of new coatings for materials such as aluminum, in which adhesion is usually a problem, requires an understanding of at least the general mechanism by which metallic coatings adhere to metals. In this paper, current theories of interfacial energy are applied to the calculation of adhesive energy and the specific case of zinc coated aluminum is discussed.

5.1.2. The Effect of Surface Energy:

As has long been known, the adhesion between two metallic surfaces is related to the surface energies of each of the two metals. Consider the total system energy of the metals in contact and compare it to the total system energy when the

metals are separated. The energy difference between the two cases is the adhesive energy per unit area given by,

$$E_{ad} = \gamma_c + \gamma_s - \gamma_i \quad [1]$$

where γ_c and γ_s are the surface energies of the coating and substrate, respectively, and γ_i is the interfacial energy.

Equation [1] does not include either plastic deformation or stored strain energy in the coating or substrate. If two

identical metals of different orientations are considered,

$$\text{then } E_{ad} = \gamma(\text{orientation 1}) + \gamma(\text{orientation 2}) - \gamma_i \quad [2]$$

Therefore, in the case of perfect autoepitaxy ($\gamma_i = 0$), equation [2] becomes

$$E_{ad} = 2\gamma \quad [3]$$

The relationship given by equation [3] would have to hold no matter where the interface was located. Therefore, equation [3], represents the cohesive energy of the material per unit area. In the case of aluminum, for example, using a bulk value for $\gamma = 840 \text{ ergs/cm}^2$, the adhesive energy from equation [3] is 1680 ergs/cm^2 . This is only an approximate value because the surface energy varies with the orientation and measured values of γ are usually an average of many orientations. If two dissimilar metals are used and γ_i is less than $\Delta\gamma$ where $\gamma_c = \gamma_s + \Delta\gamma$, the adhesive energy would always appear to exceed the cohesive energy of the material with the lower surface energy by the amount $\Delta\gamma$. Therefore, if a normal force were applied to the coated substrate, fracture would occur in

the material with the lower surface energy, and destructive measurements of adhesion, such as peel tests, would be measurements of the cohesive energies of the lower surface energy material and would not be a measurement of true adhesion.

In practice, the interfacial energy γ_i is not $<\gamma$. Calculations of adhesive energy must take into account the fact that the interfacial energy, γ_i , depends on the crystal structures of the material and the coating, the misfit between these two structures, and the stored elastic strain energy in both the coating and the substrate. The following calculations for adhesive energy make use of the theory of interfacial energy proposed by Jesser and Kuhlman-Wilsdorf (10). Calculations on the zinc-aluminum interfacial shear modulus given in Appendix I are based on data in a paper by Rudman and Averbach (11). In addition, a discussion of the effect of a pre-existing crack in the interface on adhesion is presented.

5.1.3. The Effect of Structure:

It is assumed that the potential energy variation experienced by an atom of the coating material moving along the substrate is given by a Peierls-Marbaro function as,

$$V = x V_0 \left[1 - \cos \frac{2\pi x}{x a_s} \right] + y V_0 \left[1 - \cos \frac{2\pi y}{y a_s} \right] + C \quad [4]$$

where V_0 represents the potential energy amplitude, a_s the lattice constant of the substrate, and C the potential energy/atom of a coating atom when sitting in the bottom of the potential trough. The subscripts x and y refer to the x and y directions. Under these conditions, the adhesive energy is proportional to

an average potential amplitude, $V_o = 1/2(V_{ox} + V_{oy})$, for N atoms, Van der Merwe has shown (12),

$$E_{ad} = 2 KNV_o \quad [5]$$

where for fcc materials $K = 3$. The potential V_o is related to G_o , the shear modulus of the interface as was shown by Van der Merwe as

$$V_o = \frac{G_o a_s}{(2\pi)^2 Nd} \quad [6]$$

The subscripts denoting the x and y dependence have been left out for clarity, and d is the vertical separation between the coating and the substrate. Using this expression for the average potential amplitude (6) in equation [5], the adhesive energy per unit area becomes

$$E_{ad} = \frac{K G_o a_s^2}{2\pi^2 d} \quad [7]$$

Numerical values for the adhesive energies are obtained by assuming a symmetrical x and y potential distribution and a close packed configuration with the substrate. The lattice parameter in the interface is approximated as, proposed by Jesser and Kuhlman-Wilsdorf (10) by

$$a = \frac{2a_c a_s}{a_c + a_s}, \quad [8]$$

and the interfacial shear modulus is calculated with the assumption of a linear correlation of shear modulus with bonding energy (13). Thus, through the atom spacings of the

coating and substrate, a_c and a_s , the effect of orientation has been introduced into the calculations of adhesive energy. For epitaxial deposits of zinc on aluminum (14), the adhesive energies from equation [7] are given by:

$$\text{Al}(111)//\text{Zn}(0001), E_{ad} = 1530 \text{ ergs/cm}^2$$

$$\text{Al}(011)//\text{Zn}(0001), E_{ad} = 1280 \text{ ergs/cm}^2$$

$$\text{Al}(100)//\text{Zn}(0001), E_{ad} = 930 \text{ ergs/cm}^2$$

Since the cohesive energy of zinc is in the neighborhood of 1480 ergs/cm^2 , it is seen that failure will occur within the interface on (011) and (100) aluminum planes. This calculation is only a first approximation and more exact calculations have to take into account both the existence of interfacial dislocations and their effect on bonding, and the elastic strain energy produced as a result of misfit between the coating and substrate. In the latter case, the dislocation density should be reduced. Moreover these calculations represent a minimum adhesive energy. In practice considerable work would have to be put into the lattice both in the form of elastic and plastic deformation before planar fracture would occur.

5.1.4. The Effect of Misfit Dislocations on Bonding Energy:

If a significant misfit between the crystal structure of the coating and the substrate exists, a series of interfacial dislocations will form in such a way as to minimize the resultant strain energy. The interfacial energy can now be written as

$$\gamma_i = x E_d + y E_d + CN \quad [9]$$

where C, represents, as previously discussed, the potential energy of an atom sitting in a potential trough. The number of atoms is given by N and the energy of an array of dislocations by E_d . (Note: $CN = \gamma_s + \gamma_s - 2KNV_o$.) The adhesive energy can now be written as,

$$E_{ad} = 2KNV_o - (x E_d + y E_d). \quad [10]$$

The dislocation energy per unit area was shown by Van der Merwe to be given, leaving out the x and y substrates, as,

$$E_d = \frac{G_o}{4\pi^2} \left[1 + \beta - (1 + \beta^2)^{1/2} - \beta \ln 2\beta (1 + \beta^2)^{1/2} - 2\beta^2 \right] \quad [11]$$

where $\beta = \frac{2\pi Gb}{P(1 - \nu)(1 + \frac{G_c}{G_s})G}$ and is a misfit parameter, P is

the vernier period, $a = \frac{a_s a_c}{a_c - a_s}$, and b is the Burgers vector in the interface. By introducing the effect of dislocations into the interface, it is seen that the presence of interfacial dislocation will serve to reduce the adhesive energy over the dislocation free model. The results of calculations for our special case of epitaxial coatings of zinc on aluminum are,

$$Al(111)//Zn(0001):E_{ad} = 1300 \text{ ergs/cm}^2$$

$$Al(011)//Zn(0001):E_{ad} = 1200 \text{ ergs/cm}^2$$

$$Al(001)//Zn(0001):E_{ad} = 840 \text{ ergs/cm}^2$$

5.1.5. The Effect of Strain Energy on Adhesion:

As a result of misfit between the substrate and the coating, strains will be induced in both the substrate and coating lattices, the density of misfit dislocations, if they exist, will be reduced and the adhesive bonding affected in a complex manner. In the way proposed by Jesser and Kuhlman-Wilsdorf, the new strained lattice parameters at a strain, e , are,

$$a'_c = a_c + a_c e_c \text{ and } a'_s = a_s - a_s e_s, \quad [12]$$

and the total energy is given by

$$E_{ad} = 2KNV_o - xE_d + yE_d - E_s \quad [13]$$

It was shown by Jesser and Kuhlman-Wilsdorf (10) that the strain energy, E_s , can be expressed as

$$E_s = G_c h_c \cdot \frac{x e_c^2 + y e_c^2 + 2\nu x e_c}{1 - \nu_c} + \frac{x e_s^2 + y e_s^2 + 2\nu x e_s y e_s}{1 - \nu_s} \quad [14]$$

where ν is Poisson's ratio and h represents coating thickness.

The strain, e_c of the coating is given by

$$e_c = \frac{-ba_1 \ln[2\beta' (1 + \beta^2)^{1/2} - 2\beta'^2]}{(1 + \frac{G_1}{G_2}) (a_2 + a_1)(2\pi hc)(1 + \nu)} \quad [15]$$

For a thick substrate, $e_s = 0$. As a result of strain, however, the dislocation contribution to the interfacial energy will be reduced. A new value for E_{ad} can be calculated from Equation [11] by using equation [12] to calculate new values for the misfit. For zinc coated aluminum the new values of the adhesive energy are:

$$\text{Al}(111)//\text{Zn}(0001), E_{ad} = 1300 \text{ ergs/cm}^2$$

$$\text{Al}(110)//\text{Zn}(0001), E_{ad} = 1170 \text{ ergs/cm}^2$$

$$\text{Al}(001)//\text{Zn}(0001), E_{ad} = 800 \text{ ergs/cm}^2$$

A comparison between values calculated from the above theory with results of other investigators is shown in Table I.

5.2. The Effect of a Pre-Existing Crack in the Interface on Adhesion:

A pre-existing crack in the interface can result in adhesive failure by reducing the stress necessary to propagate the crack. Such a crack can be a result of poor cleaning, blistering pores, patches of oxide or other causes. The Griffith type model considered in this calculation is shown in figure 16 and consists of a crack of length $2c$ and unit depth, located in the interface between a substrate of surface energy γ_1 , and a coating of surface energy γ_2 .

The total surface energy of the crack is then given by

$$E_s = 2c\gamma_c + 2c\gamma_s = 2c(\gamma_c + \gamma_s) \quad [16]$$

In order to find the stress, σ , at which the crack will just start to propagate, this energy is equated with the

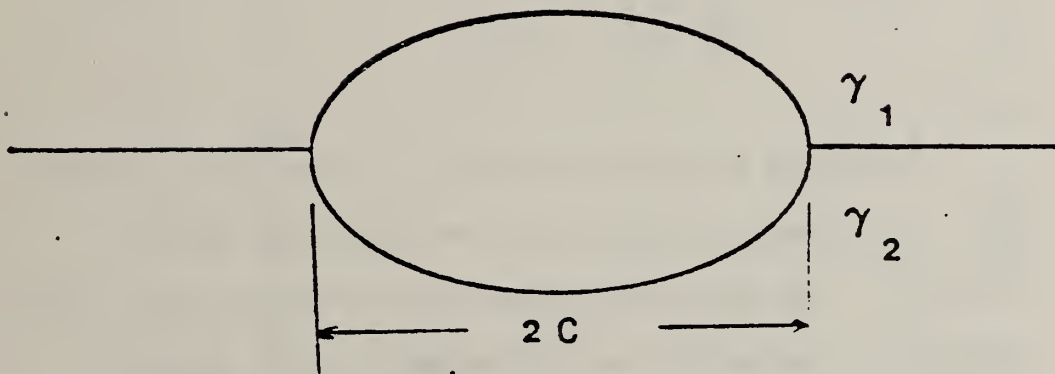


Figure 16. A model for a preexisting crack in the interface. The crack is of unit depth and of length $2C$.

stored strain energy as

$$E_{\text{surface}} = 2c(\gamma_c + \gamma_s) = E_{\text{strain}} = \frac{\sigma^2}{E_c} + \frac{\sigma^2}{E_s} \frac{\pi c^2}{2} \quad [17]$$

where E represents Young's modulus. Under equilibrium

$$\frac{\partial (E_{\text{surface}} - E_{\text{strain}})}{\partial c} = 0 \quad [18]$$

so that

$$\sigma_{\text{critical}} = \sqrt{\frac{2(\gamma_1 + \gamma_2)}{\pi c \left(\frac{1}{E_c} + \frac{1}{E_s} \right)}} \quad [19]$$

In the case of aluminum and zinc, σ_{critical} from equation [19] is plotted as a function of the crack half length in figure 17. For crack lengths less than one micron, the stress necessary to cause delamination exceeds 2×10^9 dynes/cm² (30,000 psi). For cracks in aluminum only, the stress (Griffith Criteria) is 1.95×10^9 dynes/cm² (28,300 psi) and for one micron cracks in zinc 2.2×10^9 dynes/cm² (31,900 psi). Note that once a crack has started, it may run along the interface, go into the coating or move into the substrate. A more detailed discussion of crack propagation along an interface was given by Good (4). In any case, once a crack has started to grow, the stress necessary to make it continue to grow drops off very rapidly, so that under conditions of constant stress (and

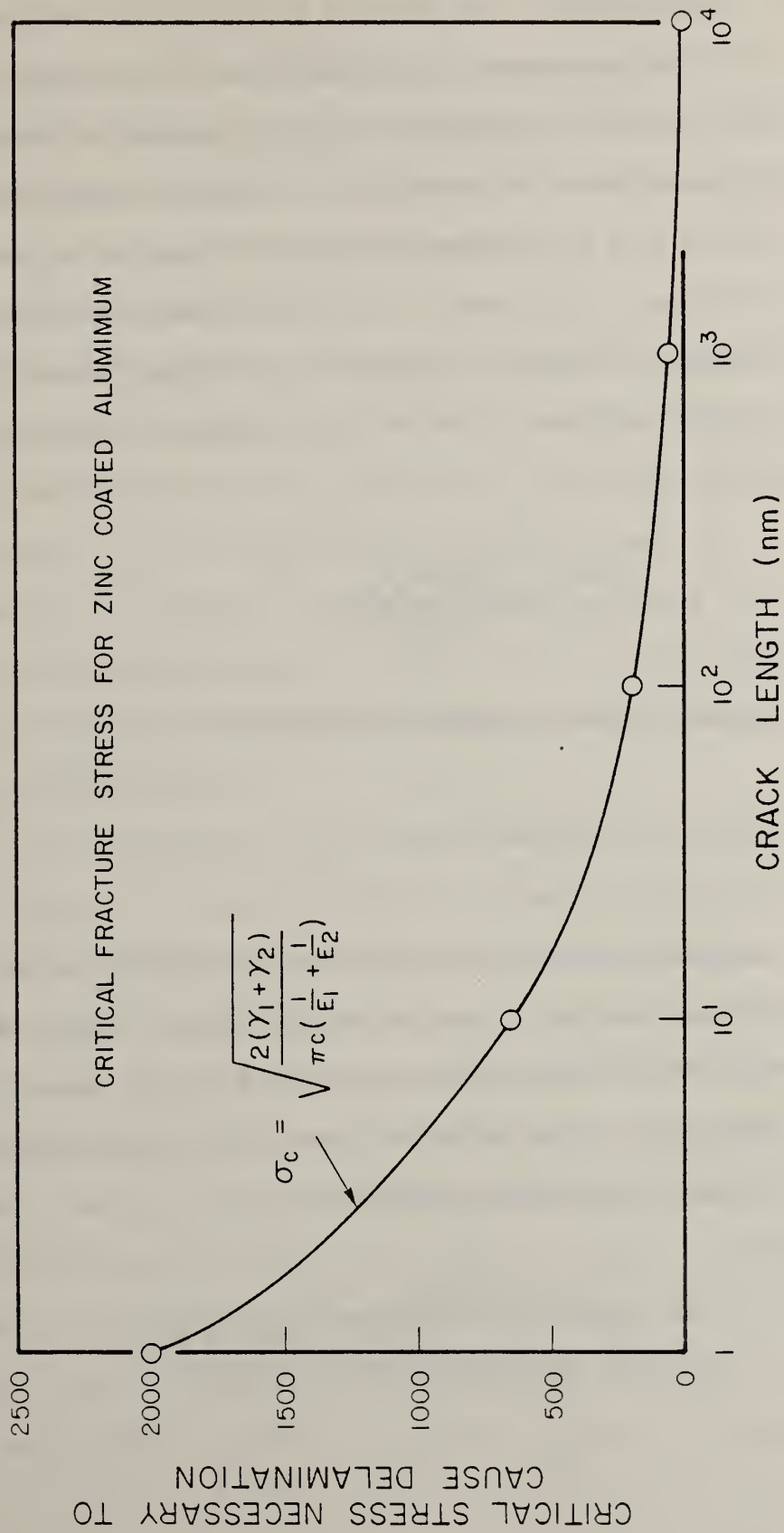


Figure 17. The critical stress required to propagate a crack in the interface for zinc coated aluminum

constant crack radius) the coating will delaminate.

5.3. Psuedomorphism: the critical radius and the critical thickness:

The phenomenon of pseudomorphism refers to the tendency of a coating to assume the crystal structure of the substrate irrespective of its own crystal structure. The stored strain energy of a pseudomorphic deposit increases with both the thickness of the deposit and with the radius of the pseudomorphic nucleus. Therefore, the deposit is limited in both the radius and the thickness. The critical radius was given by Cabrera (1) to be

$$R_c = \frac{-3b(1 + G_o a_s^2 / 4G_s a_o^2)}{2(1 + G_o / G_s)f} \quad [1]$$

where f represents the misfit given by

$$f = \frac{a_s - a_o}{a_o} \quad [2]$$

The other quantities in equation [1] were defined in the previous section. Using the values for zinc epitaxy on aluminum the critical radius was found to be 4.4 nm or about 20 atom layers thick. The critical thickness for pseudomorphism given by Jesser and Kuhlman-Wilsdorf (2) as

$$H_c = \frac{-G_2 b^2 \ln \frac{-4\pi G_1 G_2 (a_2 - a_1)}{(G_1 + G_2)G(1 - \vartheta)(a_1 + a_2)}}{2\pi a_2 f(1 + z\vartheta)(G_1 + G_2)}$$

where for the zinc-aluminum system on the (111) aluminum plane the critical thickness was found to be 0.2 nm or about 1 (at most) monolayer. These calculations seem to preclude this phenomenon of being of practical importance because crystals of zinc immersion deposited on aluminum are commonly observed as being of larger thickness and radius.

Discussion and Conclusions:

Both the existence of interfacial dislocations and the stored elastic strain energy contribute in a significant way to the adhesion of metallic coatings on crystalline aluminum substrates. For non-crystalline substrates, aluminum or otherwise, the adhesive energy for metallic coatings (both crystalline and amorphous), is higher than for the comparable crystalline material because of the higher surface energy of the amorphous material.

Calculations have been presented only for the case of zinc coatings on aluminum substrates; however, a basis exists for future calculations of the relative adhesion between nickel, iron, copper, tin and various alloy coatings to aluminum, and results for these materials will be reported in the future. It was shown above that for zinc and aluminum the greatest adhesive energy occurs when coatings are deposited on (111) aluminum compared to the other principle planes. In general however, the adhesive energy will vary with the surface energy so that for fcc materials the adhesion will decrease in the following order: $E_{ad}(110) > E_{ad}(100) > E_{ad}(111)$. Moreover

from equation [7], it is predicted that the higher index planes (greater surface energy planes) would exhibit greater adhesion than the principle planes. Since extruded parts can be made in thicker cross section than the comparable rolled sheet, the incentive of improved adhesion may make a change to extrusions desirable.

In Table I a comparison between the adhesive energy determined by a number of different techniques is presented. The definition of adhesive energy used by Ferrante and Smith differs from the definition used in this paper by exactly a factor of two. When allowance is made even for this, the adhesive energies are still below these calculations by a factor of about 20 percent. It should be noted that Ferrante and Smith did not take into account the lattice mismatch between the zinc and the aluminum, nor did they take into account the stored strain energy. These factors would have reduced their values even further.

The surface energy of alloys is in general greater than the surface energy of pure aluminum and is proportional to the ultimate tensile strength. It would then seem that adhesion on alloys would be proportionally greater than on pure aluminum. This does not seem to be the case, however. One, therefore, draws the conclusion that this discrepancy is the result of either incomplete coverage of the surface, due to incomplete oxide removal, or defects in the zinc layer resulting in the existence of a crack. One cause of this, would be incomplete coverage over alloying constituents.

Table 1. Adhesive Energy for Various Coating - Substrate Combinations (ergs/cm²)

Substrate	Coating	$\chi_c + \chi_s$	Ferrante and Smith ²	E_{ad}	$-E_d$	$-E_s$	E_{total}	Experiment: Rabinowicz ¹⁵
Al	Al	1680	405	934	-	-	934	900
(100)	Zn	1580	360	928	87	30	811	900
(110)				1283	85	30	1168	
(111)				1531	200	30	1301	
Al	Mg	1390	320	813				
Al	Cu	1940		1175				
Al	Ni	2590		1517				
Zn	Zn	1480	320	1332				5700
Zn	Mg	1290	285					
Mg	Mg	1100	255	690				
Ni	Ni	3500		2040				1750
Ni								
(100)	Cu	2850		1723	164	0	1559	
(110)				2100	98	0	2000	
(111)				2226	114	0	2112	
Cu	Cu	2200	320	1070				2333

REFERENCES

1. D. H. Buckley
Proceedings of the Conference on Physics of Adhesion
Karlsruhe (1969).
2. J. Ferrante and J. R. Smith
Sur. Sci., 38, 77 (1973).
3. J. J. Bikerman
J. Coll. Sci., 2, 163 (1947).
4. R. J. Good
J. of Adhesion, 4, 133 (1972).
5. D. V. Keller
J. of Wear, 6, 353 (1963).
6. M. E. Sikoski
J. of Wear, 7, 144 (1964).
7. H. Krupp
Advan. Collid Interface Sci., 1, 111 (1967).
8. R. Eley
Adhesion, Oxford Press (1961).
9. R. E. Baier, E. G. Shafrin, W. A. Zesiman
Science, 162, 1360 (1964).
10. W. A. Jesser and D. Kuhlmann-Wilsdorf
Phys. Stat. Sol., 19, 95 (1967).
11. P. S. Rudman and B. L. Averbach
Acta Met., 2, 576 (1954).
12. J. H. Van der Merwe
J. Appl. Phys., 34, 117 (1963).
13. L. E. Murr
Interfacial Phenomenon in Metals and Alloys
Addison-Wesley Publishing Co. (1975).
14. D. S. Lashmore
J. Electrochem. Soc., 127 (1980).

LIST OF FIGURES

1. Adhesion as a function of applied voltage for phosphoric acid anodized 7146-T6 aluminum.
2. The cell and pore diameter as a function of applied voltage.
3. Adhesion as a function of pore diameter.
4. TEM micrograph of 7129-T63 anodized in three percent phosphoric acid, then plated with nickel.
5. A TEM micrograph of 7129-T63 showing growth of the anodic oxide along dislocations.
6. TEM micrograph of nickel plated into a porous anodic oxide showing pore branching.
 - a. Low magnification bright field image.
 - b. High magnification bright field image.
 - c. High magnification dark field image.
7. TEM micrograph of the initial stages of anodic film formation on 7146-T6 with the electron beam perpendicular to the interface.
8. TEM micrograph showing dissolution of the aluminum around the outside of an established pore rather than through its center as in the classical model.
9. A TEM micrograph of 7129-T63, not nickel plated, and oriented so that the electron beam is perpendicular to the interface. Note this micrograph is at a latter stage of growth and shows some structure to the cell walls.
10. A TEM micrograph showing a transition between the initial large number of very small pores formed at low voltage to the larger diameter pores present at equilibrium.
11. A Schematic Diagram of pore formation on 7000 series alloys. (Initial stage).
12. A Schematic Diagram of a mature pore structure on 7000 series alloys (probably not alloy dependent).
13. Scanning voltammetry curves for 60 °C phosphoric acid (3 percent) on three representative alloys.
14.
 - a. Scanning voltammetry curves for the ASTM I zincate electrolyte on 99.99 percent aluminum.
 - b. Scanning voltammetry curves for ASTM II zincate electrolyte (same as a 14a with ferric chloride and Rochelle salt).
 - c. Scanning voltammetry data for the double zincate procedure (second zinc immersion).
15. Dissolution data (a - h) each figure labeled separately.

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBSIR 80-2142	2. Gov't. Accession No.	3. Recipient's Accession No.
4. TITLE AND SUBTITLE Anodizing and Immersion Processes		5. Publication Date November 1980	
		6. Performing Organization Code	
7. AUTHOR(S) Dr. David S. Lashmore		8. Performing Organ. Report No.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, DC 20234		10. Project/Task/Work Unit No.	
		11. Contract/Grant No.	
12. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP) Aluminum Association, Inc. 818 Connecticut Avenue, N.W. Washington, DC 20006		13. Type of Report & Period Covered	
		14. Sponsoring Agency Code	
15. SUPPLEMENTARY NOTES ☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.			
16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.) This report summarizes results on the "Plating on Aluminum" project, which was sponsored by the Aluminum Association. The program includes both anodizing and immersion pretreatments as well as a discussion of adhesion. In addition to the summary of results, some details of the last seven months of the project are presented including: (a) the morphology of the initial stages of anodic film formation; (b) the morphology of the interface of nickel coated anodized aluminum; and (c) a discussion of adhesion.			
17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons) Adhesion; anodizing; coatings; electrodeposition; immersion deposition; plating; plating on anodized aluminum			
18. AVAILABILITY ☒ Unlimited ☐ For Official Distribution. Do Not Release to NTIS ☐ Order From Sup. of Doc., U.S. Government Printing Office, Washington, DC 20402, SD Stock No. SN003-003- ☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161		19. SECURITY CLASS (THIS REPORT) UNCLASSIFIED 20. SECURITY CLASS (THIS PAGE) UNCLASSIFIED	21. NO. OF PRINTED PAGES 63 22. Price \$7.00

